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ELECTRON DIFFUSION, ELECTRON ATTACHMENT, AND THE AGING OF NEGATIVE IONS IN COMMERCIAL NITROGEN AT ATMOSPHERIC PRESSURE.

BY

JOHN ZELENY, Ph.D.,

Yale University.

ABSTRACT.

A criticism by Loeb and Bradbury of my interpretation of the experimental results of that part of a previous paper which dealt with the aging of negative ions in commercial nitrogen is shown to be invalidated by a mistake in their analysis and by assumptions which do not represent facts with sufficient accuracy. A more extended analysis of the previous work and new evidence which is given confirm the correctness of the former contention that the negative ions in question changed in size with age. The lateral spread, owing to diffusion, of a stream of electrons in this nitrogen at atmospheric pressure, when moving in an electric field of about 100 volts/cm., was found to be very nearly the same as that for positive ions under like conditions. The average energy losses of the electrons at collision with the molecules must therefore have nearly balanced the gains from the electric field and hence were greater than would result from purely elastic collisions. The experimental results indicate that in fields down to at least 20 volts/cm. nearly all of the attachment of electrons to molecules in the gas used occurred close to the place of their liberation.

In a recent paper [1] on the aging of ions in air and nitrogen, I reported among other results some observations on the mobilities of negative ions in nitrogen containing about 0.3 per cent. of oxygen. I interpreted my results as showing that

[1] J. Zeleny, *Phys. Rev.*, 38, 969 (1931).

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

these ions, after being formed by the attachment of electrons to neutral molecules of the gas, increase in size with time and that eventually a number of different sizes are present at the same time. Loeb and Bradbury,[2] in the February number of this Journal, make an extended analysis of the problem from which they conclude that it is possible to assign to my results a different interpretation than that which I gave. I propose to show that their argument is invalidated both by a mistake which they made in the derivation of one of their equations and by two assumptions in their analysis which misrepresent facts, as far as these are known, in too large a measure to permit any definite conclusion regarding my experiments to be drawn from their work.

These authors do not appear to be cognizant of some of the contents of my paper. They are under the impression that I used here the same procedure which I had employed previously [3] in the study of aged ions and subject the procedure to criticism, whereas it was not used and obviously is not suited to the study of ions of short age. Thus they speak on page 184 of their paper of "the circular ring of holes admitting ionized gas from outside the cylinder"; on page 191 of "aging and attachment in the ionization space outside the cylinder"; and on page 192 of "the variable initial state of the attachments for the carriers coming through the holes with different air current velocities in Zeleny's measurements." As a matter of fact, there were no holes in the outer cylinder through which gas could pass, and the ions on which measurements were made were produced just inside of the cylinder and not outside of it. I showed the details of the new arrangement in Fig. 1 on page 970 of my paper and definitely stated there that "Alpha-rays from the polonium produce ions in the air stream close to the inner surface of the outer cylinder, after passing through aluminum covered, 1 mm. wide openings made in that cylinder along a circumference."

On page 193, Loeb and Bradbury use the phrase, "the peculiar mobility scale for downstream distance . . . ." What is there "peculiar" about a relation in which the

[2] L. B. Loeb and N. E. Bradbury, JOUR. FRANKLIN INST., **213**, 181 (1932).
[3] J. Zeleny, *Phys. Rev.*, **34**, 310 (1929).

mobility varies inversely as the distance? How could the relation be more simple?

Again, on page 184 they state, "However, the ionizing source used by Zeleny precludes any very accurate comparison of theory and experiment . . . ." Wherein was my source defective? Are they not confusing here too the present source with the one used previously? In the present case the ionization occurred in the measuring field itself and in a region but one millimeter wide, so the source was actually a very suitable one for making a comparison between experiment and theory. More knowledge on related matters is needed, however, before a comparison of the kind attempted by the above authors can have any real value.

Before taking up the criticism of Loeb and Bradbury's analysis, I propose to consider in more detail than was previously done the experimental results in question and to present some evidence which they furnish regarding electron diffusion and the attachment of electrons to molecules. This procedure will elucidate the problem in hand and make manifest the reasons for concluding that negative ions in commercial nitrogen undergo change with time.

The negative carriers in my experiments started their journey, as free electrons of very high mobility, from the neighborhood of the inner surface of the outer of two co-axial cylinders. While they were crossing the space between the two cylinders some of the electrons became attached to molecules, forming the ions under investigation. During the rest of their passage, these ions were blown down stream by a slow non-turbulent current of gas and reached the inner cylinder at different points along its length. Aside from the potential on the outer cylinder and the magnitude of the gas stream, the point where any particular ion impinges on the cylinder is determined by the radial position from which it started, by its mean mobility, and by any chance wandering from its path it may have suffered because of its motion of thermal agitation. Owing to this last element, there are some parts of the cylinder which receive not only ions but also electrons that have not undergone attachment. The experimentally determined distribution curve is then in general a composite of two curves, one giving the distribution of ions and the other

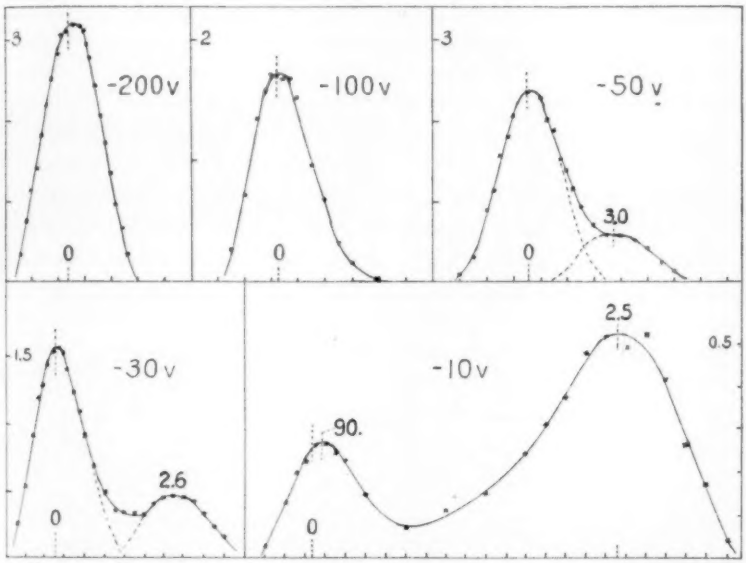
of electrons. In order to study the relative positions of the ion peak on the distribution curves obtained with different potentials on the outer cylinder, I chose to assign to each peak a so-called "peak mobility," meaning here by that term the mobility an unchanging ion starting from the origin would have to possess in order to reach the inner cylinder at the position indicated by the summit of the peak in question.

It was found that with − 200 volts on the outer cylinder the carriers all had such a large velocity that the summit of the distribution curve was deflected so very little by the slow gas stream that only a rough estimate of their peak mobility could be obtained. As the voltage on the cylinder was reduced by steps, a larger and larger portion of this group of fast carriers, which apparently were free electrons for all or a greater part of their paths, became transformed into the much slower ions. With − 10 volts on the cylinder about four-fifths of the final carriers consisted of slow ions. The curves in Fig. 1, taken from my previous paper, show the distributions of ions on arrival at the inner cylinder for a number of different voltages on the outer cylinder, the ordinates giving the ion currents reaching a narrow section of the inner cylinder when placed at different positions which are indicated by the abscissas of the curves. The divisions shown on the axis of abscissas represent millimeters in each case. The short vertical broken line marked by O shows the position on each curve of the peak of a separate distribution curve obtained when no gas stream was flowing between the cylinders, and it is from this line that the deflection of the ions by the gas stream is to be measured.

As stated in my paper, the nitrogen used in my experiments was commercial gas prepared by the Linde process. I was assured by the firm which supplied the gas that great care was used to obtain a uniform product and that I could rely on the percentage of oxygen present in different tanks as being close to 0.3 per cent. Nevertheless, for the lowest of the voltages used, where the electric carriers moved least rapidly through the gas, the results obtained with gas from different tanks were not exactly alike. Differences larger than observational errors were found in the ion peak mobilities for the same voltage on the outer cylinder and the fraction of

the electrons which had become attached under like conditions in crossing also was not always identical. However, when gas from any one tank was being used the curves for different voltages showed the same general changes typified by the curves of Fig. 1, although with − 10 volts a more simple type of curve than that given was at times obtained and this will be shown in Fig. 3. I emphasize this fact that the individual curves were not exactly reproducible for different samples of gas to show that they may not be used

FIG. 1.



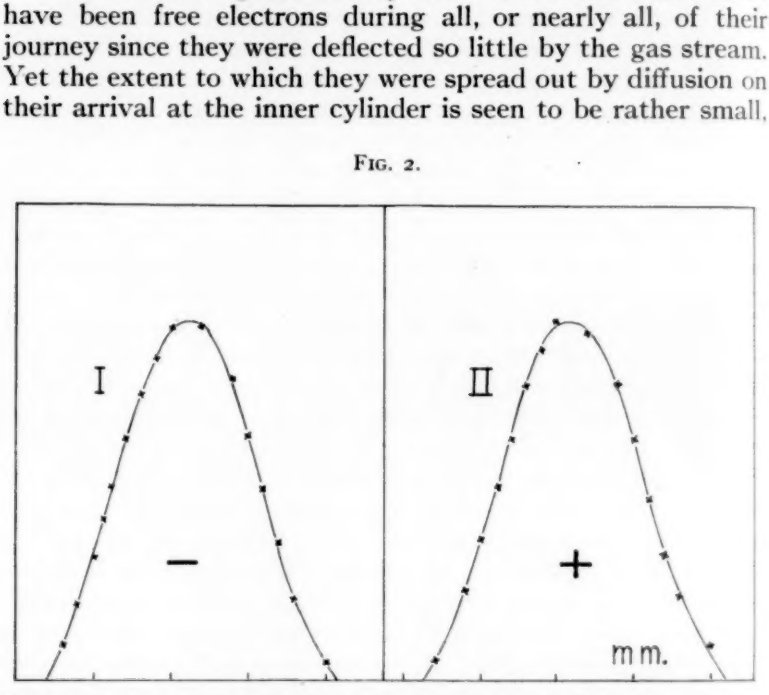
Distribution of negative ions in nitrogen on arrival at inner cylinder, for different potentials indicated. Ordinates give ion currents in arbitrary units. The abscissas indicate position of ion collecting ring of inner cylinder, the divisions being millimeters. The average gas stream velocity for the 200 v., 100 v., 50 v., 30 v. and 10 v. curves was respectively 9.62, 9.41, 7.70, 7.71 and 6.07 cm./sec.

with confidence for drawing accurate conclusions regarding the probability of attachment of electrons in nitrogen containing 0.3 per cent. of oxygen. My previous paper, in which the work on nitrogen under discussion was included, had as its main theme the large influence of traces of impurities on ion growth. The work on nitrogen is in harmony with the other results there given, the effect on negative ions in the

nitrogen used being however more pronounced than that on negative ions in air. An effect of traces of impurities on the probability of electron attachment here indicated was to be expected.

The carriers represented by the − 200 volts curve must have been free electrons during all, or nearly all, of their journey since they were deflected so little by the gas stream. Yet the extent to which they were spread out by diffusion on their arrival at the inner cylinder is seen to be rather small,

FIG. 2.



Distribution curves for 200 volts, with gas at rest. Curve I gives distribution of electrons on reaching inner cylinder, and curve II gives the distribution of positive ions.

especially when account is taken of the fact that 2.9 mm. of the observed spread arises from the combined widths of the ion source and that of the ion collector ring. This result makes it of interest to compare the amount of spreading of a beam of electrons with the spreading under like conditions of a beam of positive ions. Such a comparison is shown in Fig. 2, the distribution curves for which were obtained while the gas was at rest, one with − 200 volts and the other with + 200 volts on the outer cylinder. It is seen that the lateral spread in curve II for positive ions is nearly the same as that in

curve I where the carriers were electrons. Actually the total spread of the ions was found to be on the average a few per cent. larger than that of the electrons. It is possible that this behavior was due to mutual repulsion whose influence may have been appreciable for ions only, owing to the greater charge density present with ions than with the more fleet electrons. The result, that the lateral spreading of a swarm of electrons in passing through a given electric field is no greater than that for ions under similar conditions, appears to be opposed to a current belief that the diffusion effects of electrons in such cases are much larger than those of ions. However, all previous measurements of diffusion effects of electrons have been made at gas pressures much smaller than those which I used. In a former paper [3] I gave a formula, which was found in good agreement with experiment, in which the spread of ions by diffusion with time t is given as a function of Dt, where D is the coefficient of diffusion. In general it may be said that where electric carriers have a large coefficient of diffusion their mobility is also large and hence the time taken by them to cross a given distance in a given electric field is correspondingly small so that the product Dt, and therefore the total lateral spread of the carriers during their passage, is independent of the nature of the carrier. This relation holds only as long as the ions are, at least approximately, in thermal equilibrium with the molecules of the surrounding gas. Electrons do not in general satisfy this condition since Townsend [4] has shown that in an electric field an electron may acquire an energy greatly in excess of that possessed by a molecule of the surrounding gas. Working with dry air at a few millimeters pressure, he found that the lateral spread of a beam of negative ions (here doubtless electrons) was much larger than that of a similar beam of positive ions. However, Townsend's results show that for any given value of the electric field the excess of lateral spread for electrons over that for positive ions diminished quite rapidly with increase of pressure even over the small range of 5.5 mm. to 16.5 mm. that he used. His results are therefore not necessarily in conflict with my observations in

[4] J. S. Townsend, *Proc. Roy. Soc.*, **81**, 464 (1908).

which I found in nitrogen at atmospheric pressure that the lateral spread of electrons in moving through a given electric field was no greater than that of positive ions. My observations, discussed above, lead to the conclusion that in commercial nitrogen at atmospheric pressure, even in electric fields as high as 100 volts/cm., electrons do not acquire an energy which is much in excess of that possessed by molecules of the gas. The collisions between electrons and the molecules of the gas cannot therefore be of a perfectly elastic type, because computation shows that on the supposition of such elastic collisions the limiting energy acquired by electrons under the conditions named would be several times as large as that possessed by the surrounding molecules. Franck and Hertz,[5] and Townsend and Bailey [6] also concluded from their experiments that electrons, when moving in an electric field, on collision with hydrogen molecules lose larger portions of their energy than the laws of perfectly elastic collision require.

There is some interest in the fact that in the nitrogen here used, which contained an appreciable amount of oxygen, free electrons were present in large numbers in the gas at atmospheric pressure even in the fairly weak fields of a few volts per centimeter. Franck [7] in his early measurements, in which he observed abnormally high mobilities for negative ions in pure nitrogen, found that the electrons all disappeared when the commercial gas used was not specially purified. Townsend and Tizard,[8] however, observed free electrons even in dry air with its high oxygen content, provided the quotient of the electric field in volts per centimeter by pressure in millimeters was above 0.2. An explanation of the disappearance of the electrons in Franck's experiments is assigned to his use of a sinusoidal field in which, during each cycle, the electrons momentarily found themselves in a very weak field at which time their attachment to molecules is thought to have taken place.

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[5] J. Franck and G. Hertz, *Verh. d. D. Physik. Ges.*, **15**, 373 and 613 (1913).
[6] J. S. Townsend and V. A. Bailey, *Phil. Mag.*, **42**, 873 (1921).
[7] J. Franck, *Verh. d. D. Physik. Ges.*, **12**, 613 (1910).
[8] J. S. Townsend and H. T. Tizard, *Proc. Roy. Soc.*, **A88**, 336 (1913).

The work of Bailey [9] and that of Cravath [10] on the attachment of free electrons in air shows that for low fields the probability of attachment of an electron, at impact with a molecule, increases very rapidly as the strength of the field is decreased. Electron attachment data are not available for conditions approximating closely to those of my experiments, the results of Cravath in air at 120 mm. pressure approaching my conditions the nearest, even though the oxygen percentage is over sixty times as large, the pressure less than one-sixth and data are not given for values of the ratio of field (X) to pressure (p) as low as those I used. Nevertheless, at the lowest values of X/p given, Cravath finds the probability of electron attachment to be increasing very rapidly with decrease of X/p and it is therefore probable that in any one of my experiments the probability of attachment near the surface of the outer cylinder where the electrons were liberated was a great many times larger than near the surface of the inner cylinder where the field was about three times as large, and that even a larger variation existed between experiments done with different voltages. Cravath's results would therefore lead us to expect a rapid decrease in the number of new ions formed by electron attachment on proceeding from the outer cylinder to the inner one. The experimental evidence indeed indicates (see below) that for all except the lowest voltages used on the outer cylinder the larger part of the electrons which became attached to molecules actually did so near the place of their liberation. Since the ionization of the nitrogen was produced by alpha rays at the end of their ionizing range, it is possible that many of the electrons were ejected from the molecules during the ionization process with velocities equal to or below that most favorable for electron attachment. Such a condition would conspire with the low electric field to localize the region where most of the ions are formed. Wellish also concludes from his recent experiments in air [11] that the great

[9] V. A. Bailey, *Phil. Mag.*, **50**, 825 (1925).

[10] A. M. Cravath, *Phys. Rev.*, **33**, 605 (1929). In Loeb and Bradbury's paper the volume references to this paper and two of Bailey's papers are incorrectly given.

[11] E. M. Wellish, *Proc. Roy. Soc.*, **A134**, 427 (1931).

majority of the negative ions which had formed from photo-electrons had done so in the vicinity of the electrode at which the electrons originated. Bailey [12] however says Wellish's results are not in agreement with his own and states that electron attachment in the gas is of importance, although attachment at the electrode was not directly studied by him.

The experimental evidence to which reference has just been made is to be found in ion distribution curves like the ones for − 30 volts and for − 50 volts shown in Fig. 1. It is seen that the compound curve for − 50 volts for example may be considered to result from the superposition of the two simple symmetrical distribution curves indicated by broken lines. The left one of these curves represents electrons which have crossed the field without permanent attachment. The right hand curve represents ions. This ion curve is symmetrical about a vertical axis and its base is approximately of the same width as that of the electron curve. Since it was shown above (see Fig. 2) that the lateral spread produced by diffusion of a stream of ions and of electrons after moving a given distance in the same electric field is nearly the same, these characteristics of the ion curve indicate that the ions must have originated for the most part in the same locality. The only possible place of this common origin is the region near the surface of the outer cylinder where the ionization of the gas occurred and where the probability of electron attachment to molecules has the highest value since the field there is the weakest. It might be urged that the subdivision of the − 50 volts curve into the two symmetrical components shown was an arbitrary procedure. What was actually done was to draw first the symmetrical electron curve, using for a guide a curve obtained from a separate set of observations in still gas. The second or ion component curve was then obtained by simple subtraction. Naturally this process is not so exact, even when done with large scale drawings, but that some variation could be made which would be consistent with the observations and show for example a tailing off of the ion curve to the left. It is found by trial, however, that only a small variation of this kind is really permissible

[12] V. A. Bailey, *Nature*, **129**, 166 (1932).

if adherence is made to a symmetrical electron curve and an ion curve which does not show a sudden change of direction. Moreover, it will be shown below that, when allowance is made for the effects of diffusion, the place of landing of those ions which were carried farthest down stream coincides with the summit of the ion peak given in the figure, so that the great majority of the ions actually came from a region which did not extend far from the surface of the outer cylinder. Ions originating at intermediate points between the cylinders would have the effect of broadening the ion distribution curve and displacing its peak to the left.

In my previous paper, the fact that the peak mobility of the ion curves decreased with reduction of the voltage applied to the outside cylinder was taken to indicate that these negative ions increased in size with age. In the brief space there devoted to this subject, I gave no argument in support of this statement. I shall proceed to do so now. The − 50 volts curve of Fig. 1, as has been pointed out, shows that the negative ions present started for the most part from the immediate neighborhood of the surface of the outer cylinder and were spread out along the inner cylinder on arrival there owing to diffusion alone. The mobility computed from the summit of the curve therefore gives the real, mean mobility of the ions. Suppose that with − 10 volts on the cylinder the ions had also all started from the same region and that they had the same average mobility as in the case just considered. A distribution curve would have resulted, from the peak of which the computed mobility would have come out the same as before. Now suppose that to this distribution ions are added having the same mobility but which began their journey from various points between the two cylinders. These ions will not be carried down stream as far as the group first considered and their effect on the ion distribution curve will be to move its peak to the left. The mobility computed from the new location of this peak would therefore be greater than that obtained before. Since the peak mobility obtained from the actual − 10 volts curve was decidedly smaller rather than greater than that computed from the − 50 volts curve, it was concluded that the ions in the two cases could not have had the same mobility, and that the average mobility

had in reality decreased with increase of the time taken for the ions to make their journey. Even if in the − 50 volts case electron attachment had taken place to an appreciable degree along the whole path, still the shape of the − 10 volts curve shows that the amount of such attachment was there much larger and consequently the ions starting from intermediate points between the cylinders in this case would again have the effect of moving the peak of the distribution curve farther to the left than was the case for the − 50 volts curve. The conclusion must be drawn, therefore, that the down stream displacement of the ion peaks with reduction of voltage used is good evidence that the average mobility of these ions actually decreased with age.

An additional argument in support of this view which makes no reference to ion peaks will now be given. To demonstrate that the mobility of these ions changed with time it will be sufficient to show that the mobility of the slowest group of ions present diminished as the voltage applied to the outside cylinder of the apparatus was decreased. The mobility measured is of course the mean mobility found from the time it takes the ion to cover the distance between the cylinders. The age of the ions may be expressed in terms of the total time required for the ions to make the passage, although they naturally started their journey at zero age. The mobility of the slowest ions present, under any of the conditions used, may be obtained from the appropriate ion distribution curve by the following method. Ions which are all alike when they start from a small region near the surface of the outer cylinder and undergo similar changes during their journey will reach the surface of the inner cylinder spread out by diffusion over a certain length of that cylinder which is approximately equal to the length obtained for a like voltage when the carriers are electrons, as has already been shown. The width of an electron distribution curve for any voltage may be found from the compound distribution curve for that voltage, since it is essentially twice the abscissal distance between the summit of the electron peak of that curve and the left hand foot of that peak. If now from the right hand foot of the compound ion distribution curve in question a distance to the left is measured equal to half of

the spread for the electron peak, the place of landing is found for the slowest of those ions which started their journey in the ionization region at the surface of the outer cylinder and suffered no displacement by diffusion. Such a procedure applied to the − 50 volts curve of Fig. 1 for example locates this landing point at the center of the lower of the two simple symmetrical distribution curves into which the compound curve was previously resolved by the dotted lines shown. The computed mobility for these slowest ions is in this case 3.0 cm./sec. per volt/cm. It is to be noted that the width of this lower curve is closely the same as that of the higher curve, indicating that here the ions were all of the same average mobility or nearly so, for otherwise the gas motion would have blown unlike ions down stream by different distances and the width of the ion curve would have been greater than that for the electrons.

When the above procedure was applied to the − 30 volts curve of Fig. 1 the landing place of the slowest of the ions described above was again found to correspond closely with the summit position of the lower curve which has been completed by a dotted line in the figure. The computed mobility for these ions is here only 2.6 cm./sec. per volt/cm. The disagreement between the mobilities of the slowest ions present for these two voltages shows that a real change with time has taken place at least in some of the ions. The two simple curves indicated by dotted lines on this curve do not here add up to the compound curve. It is not possible to tell whether the remnant is due to ions of somewhat higher mobility than that of the ions in the lower of the curves shown or whether it represents ions which had been formed by electron attachment after these latter had completed a part of their journey between the cylinders.

The curve for − 10 volts in Fig. 1 shows that in this case the larger part of the electrons have become attached to molecules to form negative ions. Some of the ions have been carried down stream far enough to make it necessary, in applying the method of analysis used above for finding the mobility of the slowest ions present, to ascertain whether, owing to the obliquity of their paths, ions starting at one place reach the inner cylinder spread out by diffusion over a

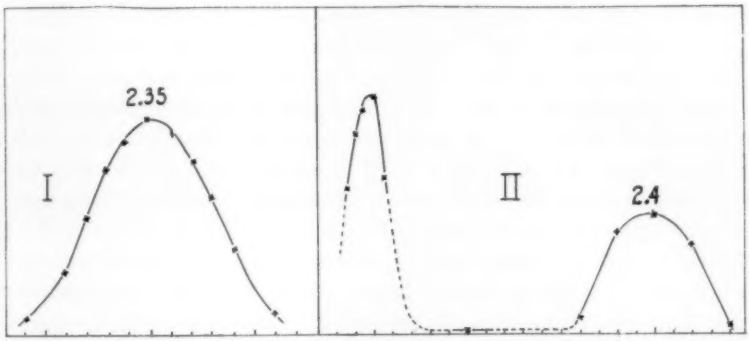
larger length of that cylinder than is normally the case. I explained in detail in a previous paper [3] how this can be done. When the method there given was applied here the correction was found actually to be almost negligibly small. The mobility obtained for the slowest of the ions which started from the proximity of the outer cylinder was found to be 2.2 cm./sec. per volt/cm. This value is lower than the 2.5 value given for the peak mobility of the curve, and hence either ions of higher mobility were present in considerable number, or many of the ions were formed by electron attachment along the path between the cylinders, or both conditions prevailed at the same time. Since the fields in the apparatus were in this case the lowest of those used, the probability of electron attachment at places removed from the surface of the outer cylinder was here greater than when the larger voltages were employed.

It should be noted that two other curves obtained with − 10 volts on the outer cylinder with gas taken from different tanks did not have the same shape as the one shown in Fig. 1, while in another sample of gas the curve obtained with − 20 volts did have the same characteristics as the above curve except that only about a half of the electrons had been transformed into ions. As already stated, differences of this kind, which appear with the lower voltages used where the time involved is not too short, point to a large influence of small traces of impurities in the gas both on ion growth and on attachment of electrons to molecules during their motion through the gas.

The two − 10 volt curves mentioned above are reproduced in Fig. 3. In curve I only the down stream portion was obtained and this is seen to be a fairly complete, symmetrical curve with a peak mobility of 2.35 cm./sec. per volt/cm. In curve II a weak ion source was used and a few readings only were taken for getting a general survey of the ion distribution along the inner cylinder of the apparatus. The electron peak appears distinctly separated from the ion peak, with few, or no, ions between. The peak mobility for this ion peak was determined as 2.4 cm./sec. per volt/cm. The ion peaks on both curves are far too wide at their bases to represent the distribution of ions of a unique mobility. Moreover,

ions produced by electron attachment along the whole path could not possibly give rise to ion distribution curves like the two here shown which are almost, if not completely, separated from the accompanying electron peaks and which are symmetrical about a vertical axis. Indeed, curve I in Fig. 3 has the same appearance as some of the curves previously obtained with aged ions which all entered the condenser through holes in the outer cylinder and which were found to have mobilities that were not all alike.

FIG. 3.



Incomplete distribution curves for − 10 volts with different samples of gas. Curve I shows the ion portion only, while curve II shows both the ion and electron portions.

The above considerations, I feel, justify the conclusion in my previous paper that the negative ions in the commercial nitrogen used increased in size with time and eventually comprised a number of different sizes. The mobility of the slowest ions present has been shown to have decreased from 3.0 to 2.2, as the time required by the ions to cross the condenser was increased from 0.04 sec. to 0.27 sec.

Coming then to a consideration of Loeb and Bradbury's analysis, these authors attempt to show that curves, qualitatively of the same general shape as mine and having ion peaks whose relative position is displaced down stream on reduction of the electric field used, can be obtained solely on the basis of electron attachment taking place along the whole path between the two cylinders, without the necessity of assuming a change of mobility with age. It is obvious, and

was obvious to me from the start, that an extended form of ion curve would result if electron attachment occurred along the whole path, whether the ions so formed all had the same mobility or not. Special significance as regards ion stability is attached therefore not to the general form of the curves but to alterations in them produced by changes in applied voltage. I have given above evidence for believing that the observed shift in the position of the summit of the ion peak with change of voltage indicates an actual decrease of mobility with time. I have also shown, without making use of the ion peaks, that the mobility of the slowest ions present decreases with the age of the ions. Moreover, it appears that for the higher fields used most of the ions were formed from electrons near the surface of the outer cylinder. Loeb and Bradbury, by aid of a formula which they derived on the assumption of a unique ion mobility, have constructed distribution curves for two voltages by adding ion distribution curves to electron distribution curves. These curves show a similarity to some of my experimental curves.* Their 90 volts curve they regard as being quite similar to my 50 volts curve, and their curve for 30 volts as being intermediate between my 30 volts and 10 volts curves. The disparity between the voltages on the curves compared presents no difficulties to these authors inasmuch as they admit that they have made several simplifying assumptions and are of the opinion that a critical study of the problem is almost hopeless. Nevertheless, in spite of these admissions, they stress the point that the peak mobility computed from their 30 volts curve is 5 per cent. smaller than that computed from their 90 volts curve, and conclude from this that the shifting of the peaks in my distribution curves was determined by the electron attachment process rather than by a change of ion mobility with age. It seems inconsistent to attach importance to this small effect when differences of several-fold have been neglected in some of the quantities appearing in their formula. In any case, I have given an argument above showing that if a unique ion mobility is assumed and more electron attachments take place in the space between the cylinders for 10 volts than for

* In the curve shown in their Fig. 2 an error has been made in the addition of the ordinates between $l = 2$ and $l = 3$.

50 volts, as the experimental curves indicate, then the peak mobility for the ions in the 10 volts curve should have been higher than in the 50 volts curve, whereas the opposite result was found experimentally.

Before a mathematical analysis of the kind attempted by Loeb and Bradbury can be of any value for testing theories by comparing its predictions with experimental results like those of mine, it must be possible to compute what fraction of the electrons, which become attached to molecules during their journey, do so at every point of the path, since the nature of this distribution determines the resultant curve obtained. This is not now possible for, as I have said above, data on electron attachment under the conditions of my experiments do not exist, although such data as are available indicate that very likely under these conditions the probability of electron attachment increases at a very great rate with decrease of electron energy. To disregard even partly this large variation in the probability of electron attachment that is indicated, for the greatly differing fields in my experiments which varied from 149 to 2.6 volts/cm., by using a relation giving a less rapid change, as the above authors have done, seems to me to discredit completely the results obtained from these computations. Loeb and Bradbury make a further assumption that the electron mobility is constant for the different fields used, although Wahlin,[13] for example, finds in nitrogen at atmospheric pressure that the mobility changes three-fold over a range of fields less than half as large as that prevailing in my experiments. Variations of this magnitude can scarcely be neglected when the effects looked for are all of a much smaller size.

Furthermore, these authors have made a mistake of importance in their analysis. They assume, since the formula for mobility which I derived for this method of measurement reads

$$k = \frac{Q \log b/a}{2\pi Vl}$$

when an ion starting at the surface of the outer cylinder ($r = b$) reaches the inner cylinder ($r = a$) at a point l cm.

[13] H. B. Wahlin, *Phys. Rev.*, **23**, 169 (1924).

down stream, where Q is the quantity of gas flowing per sec. and V the difference of potential between the two cylinders, that a similar formula

$$k = \frac{Q \log x/a}{2\pi Vl}$$

would give the mobility when the ion starts from $r = x$. The relation is by no means so simple, for a glance at the derivation I gave [14] shows that the term $\log b/a$ enters the differential equation as a constant. The relation they should have used is obtainable from the equation of the path of an ion under the conditions of these experiments, which I gave in a previous paper [3] and which reads

$$x_1 = \frac{p}{16kV\mu}[(b^4 + r^4) \log (b/a) - 2b^2r^2 \log (r/a) - 2a^2r^2 \log (b/r) - (a^2 - b^2)(r^2 - b^2)],$$

where x_1 is the down stream distance from the origin corresponding to a radial position r, and p/μ, the ratio of pressure change per unit length of the cylinders to the coefficient of viscosity of the gas, is obtainable from

$$Q = \frac{\pi(b^2 - a^2)p}{\mu}\left[(b^2 + a^2) - \frac{b^2 - a^2}{\log (b/a)}\right].$$

I am aware of the fact that Loeb and Bradbury state in their paper that "it was felt of importance to present this analysis in order to guide future investigations by this method" and that they did not consider their analysis as more than a first approximation. It is apparent however from what I have already said that the assumptions they used and the error they made in their analysis are of such a nature that the results of the analysis have at present no practical value and hence I feel the authors were not justified, on the strength of this analysis, in saying of my work that "no importance at all can be ascribed to" the movement of the ion peak with change of voltage; that "there is no evidence from these experiments that negative ions change mobility

[14] J. Zeleny, *Lon. Phil. Trans.*, **A195**, 193 (1901).

with age"; and that "the apparent movement of Zeleny's negative ion peaks furnish[es] no information on the subject."

One more matter needs mention. I found with − 200 volts, or − 100 volts, on the outer cylinder that the distribution curve obtained had but one peak which was displaced so slightly by the slow gas stream used that the distance could not be accurately determined. A very rough estimate only of the high mobility of the carriers could therefore be obtained. Nevertheless the mobility indicated was much smaller than is possessed by electrons since these should have suffered no appreciable deflection. It seemed significant that the fast carrier curve obtained, when the voltage used was only − 10 volts, indicated a mobility of approximately the same value as that obtained with − 200 volts. Were the indicated down stream shift of this peak due to the overlapping with it of the distribution curves of ions which originated somewhere along the electron path, it was thought the shift should have been larger when small potentials were used than for the larger potentials because a greater number of ions would have been formed along the path in that case. Accordingly I sought a different explanation and reverted to the old hypothesis of an electron having momentary periods of loose attachment with molecules in consequence of which the measured mobility is greatly reduced. Such loose attachments where the impinging electron gives its energy to interatomic vibrations or to low energy transitions are not, I believe, excluded by theory. Loeb and Bradbury point out, however, that such experimental evidence as exists, which is quite fragmentary, is against the possibility of electron detachment in weak fields, and conclude that the observed displacement of the electron curve does arise from the overlapping of ion curves with this curve. My curves for the higher voltages, however, indicate an almost complete absence of ions and in other cases the ion curves do not appear to extend back as far as the electron curve summit. These facts speak against the view adopted by Loeb and Bradbury. Nevertheless I fully realize that the reason I gave in my paper (and which the above authors seem to have overlooked) for preferring the view I presented there, was based, as was stated, on meager experimental evidence.

More conclusive experiments on the subject are needed. There may be some significance in the fact that Franck,[7] using an entirely different method for his measurements of electron mobilities in nitrogen, obtained low values of the same general magnitude as the estimates I gave for the peak mobilities of the electron curves in my experiments.

Loeb and Bradbury speak of the difficulty of accurately locating the abscissa of the summit of an extended curve. It is indeed difficult to draw such a curve accurately by the usual method since small errors in the few experimental points near the top affect one's judgment unduly as to where the summit of the curve should be drawn. I have found that the points on the slopes of a curve are not only a better guide for finding the top but permit the use of a larger number of observations in the determination of its location. The method adopted is to trace the complete curve so as best to fit the observations and then to draw a number of equidistant horizontal lines which intersect both slopes of the curve. A line drawn through the bisectors of the portions of the horizontal lines intercepted by the two slopes of the curve serves as a reliable guide for locating the true position of the summit. In repeated sets of fairly good observations I have found the peak positions so located to agree well within one per cent. of the width of the bases of the curves.

SLOANE PHYSICS LABORATORY,
YALE UNIVERSITY,
June 9, 1932

THE ABSORPTION OF RADIATION ORIGINATING FROM A BEAM OF ELECTRONS IN HELIUM: A NOTE ON THE ELECTRON EXCITATION FUNCTION FOR THE SHARP SERIES OF ORTHOHELIUM.*

BY

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Communication No. 70.

When helium is excited by a weak discharge there is a sufficient number of electrons in the 2S and 2s states so that the gas can easily absorb the lines $2S - 2P$, $\lambda = 20582$ and $2s - 2p$, $\lambda = 10830$, as was shown by Paschen.[1] McCurdy[2] has found that the next lines of these series $2S - 3P$, $\lambda = 5015$ and $2s - 3p$, $\lambda = 3888$ are absorbed by excited helium. Absorption has also been found to occur for atoms in the 2P and 2p states.[3] The extent to which absorption can take place depends upon the strength of the excitation in the absorption tube. It is to be expected that for stronger excitation it should be possible to obtain absorption for many lines which end in the 2P and 2p states.

McCurdy finds in some cases that lines which have different initial levels but the same final level show large differences in amounts of absorption. This has later been confirmed by Takamine and Suga,[4] also by Levy.[5]

The present work deals with the absorption of lines ending in the 2S, 2s, 2P and 2p states, by a region in the neighborhood of an electron beam which contains a high concentration of atoms in these excited states. Results will be given for members of the principal series of orthohelium and parhelium. A comparison will be made of the different amounts of absorption for lines which have the same final level but different initial levels.

* An investigation conducted at the Bartol Research Foundation of The Franklin Institute.

EXPERIMENTAL ARRANGEMENTS AND PROCEDURE.

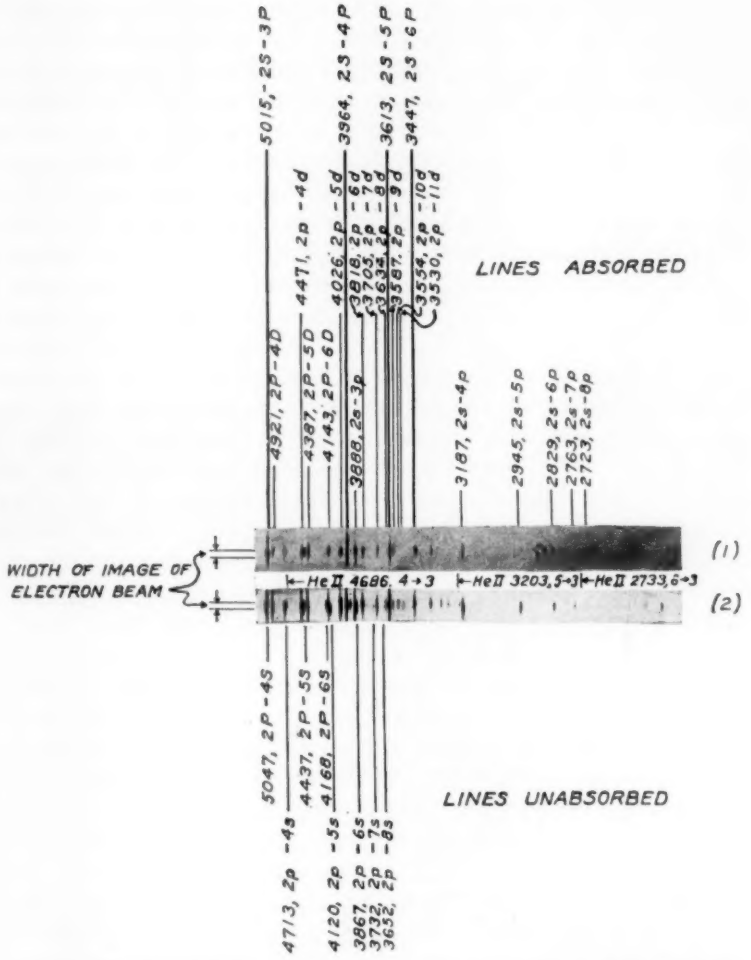
The experimental arrangement used in this work is the same as that previously described by the writer.[6] The helium atoms were excited by a sharply defined beam of electrons. The radiation originating from this small region penetrated through the gas in the tube and was finally projected on to the slit of a quartz spectrograph. The image of the beam was placed at right angles to the direction of the slit. If the radiation produced in the beam was not absorbed and re-emitted by the gas in the tube, it would produce spectrum lines whose length would correspond to the width of the image of the electron beam. However, if the radiation is absorbed and reradiated by the gas in the vicinity of the beam, then the light will become diffuse. The spectrum lines will be lengthened and they may easily become as long as the image of the slit itself.

This arrangement presents a method for correlating the length of the spectrum lines with the amount of absorption and subsequent emission occurring in the gas. The length of the lines will be used as a means for determining the relative amounts of absorption in the excited gas.

RESULTS AND DISCUSSION.

In Fig. 1 are reproduced two typical plates obtained illustrating the helium spectrum composed of lines of different lengths. The lines indicated in the upper part of the figure were found to be lines lengthened considerably beyond the boundary of the electron image, and they are interpreted as showing absorption, while the lines labeled in the lower part of Fig. 1 conformed more closely to the electron image and therefore exhibited no absorption. This is particularly true of the helium spark lines indicated at the center of the figure. Either of the two photographs can be examined to illustrate the differences in absorption. The fainter lines are difficult to see in the figure but could be plainly observed on the original plates. The helium pressure in the tube for these exposures was about 0.01 mm. of Hg. The electron current in the beam was 0.5 milliamperes, while the voltage of the electrons was 500 volts. For exposure (1) a crossfield of 160 volts/cm. was applied to the beam while for (2) this was

FIG. 1.



Reproduction of photographs obtained illustrating absorption in helium, with the long lines caused by absorption predominating.

increased to 300 volts/cm., and in a direction so as to cause the positive ions formed in the beam to move upward. It was found that the current to the edges of the slits formed by the electrodes in the tube was very small in comparison with the main current in the beam. The magnetic field was strong

enough to collimate the electrons into a sharp beam, while the diaphragms containing the slits served only for the proper placement of the electric fields. These facts preclude any possibility that the lengthening of the lines is produced by a spreading of the electron beam and not caused by absorption.

It is noticed that all of the lines of the triplet sharp series $2p - Ns$ show an elongation downwards. This displacement was produced by the action of the transverse electric field on the electrons in the beam. It has been found that when secondary electrons from the collecting electrode are permitted to enter the region of observation, they will cause a distortion of the beam when the crossfield is applied, similar to the distortion shown above. Although in the present case the secondary electrons from the collector were prevented from returning into the region photographed, the elongation observed is probably caused by slow electrons existing in the beam. The velocity of the electrons producing this effect is not known, however, it is estimated that their velocity must be considerably less than the velocity of the primary electrons. The upper part of these lines terminates sharply, corresponding to the upper edge of the electron beam, which shows that they are not absorbed appreciably by the gas. The singlet lines $2P - NS$ in Fig. 1 show, in the case of exposure (2), slight distortion, but since these lines are also terminated sharply, corresponding to the upper edge of the beam, they are not adsorbed by the gas. The distortion of these lines was eliminated by removing the electric field, in which case these two sets of lines conformed closely to the width of the electron beam, whereas the other lines designated in the upper part of Fig. 1 were always lengthened, thus showing absorption. Moreover, the distortion found above could be eliminated, while the crossfield was applied by suitably adjusting the potential of the space occupied by the electron beam.

The helium spark lines 4686A, 3203A, 2733A, and 2511A showed no lengthening due to absorption which is to be expected on account of the relatively low concentration of positive ions near the beam. The length of these lines conformed closely to the width of the electron beam, as determined by the size and shape of the effective emitting

portion of the filament. The spark lines showed an upward displacement in the direction of the motion of the positive ions which has been previously discussed.[8]

Table I contains a list of the lines examined for absorption. These are the lines obtained in spectrograms (1) and (2) illustrated in Fig. 1. In the last column are given the amounts

TABLE I.
Absorption in Helium.

Wave-length of line (Angstroms).	Transition.	Absorption determined by length of lines.	Absorption measured by McCurdy using absorption cell.
	Parhelium		
5015	2S – 3P	very strong	strong
3964	2S – 4P	very strong	weak
3613	2S – 5P	strong	very weak
3447	2S – 6P	medium	
4921	2P – 4D	medium	very weak
4387	2P – 5D	strong	none
4143	2P – 6D	medium	
4009	2P – 7D	weak	
5047	2P – 4S	none	none
4437	2P – 5S	none	none
4168	2P – 6S	none	none
	Orthohelium		
3888	2s – 3p	strong	very strong
3187	2s – 4p	absorbed	strong
2945	2s – 5p	absorbed	
2829	2s – 6p	absorbed	
2763	2s – 7p	absorbed	
2723	2s – 8p	absorbed	
4471	2p – 4d	absorbed	fair
4026	2p – 5d	absorbed	weak
3819	2p – 6d	absorbed	weak
3705	2p – 7d	absorbed	
3634	2p – 8d	absorbed	
3587	2p – 9d	absorbed	
3554	2p – 10d	absorbed	
3530	2p – 11d	absorbed	
3512	2p – 12d	absorbed	
4713	2p – 4s	none	none
4121	2p – 5s	none	
3867	2p – 6s	none	
3732	2p – 7s	none	
3652	2p – 8s	none	

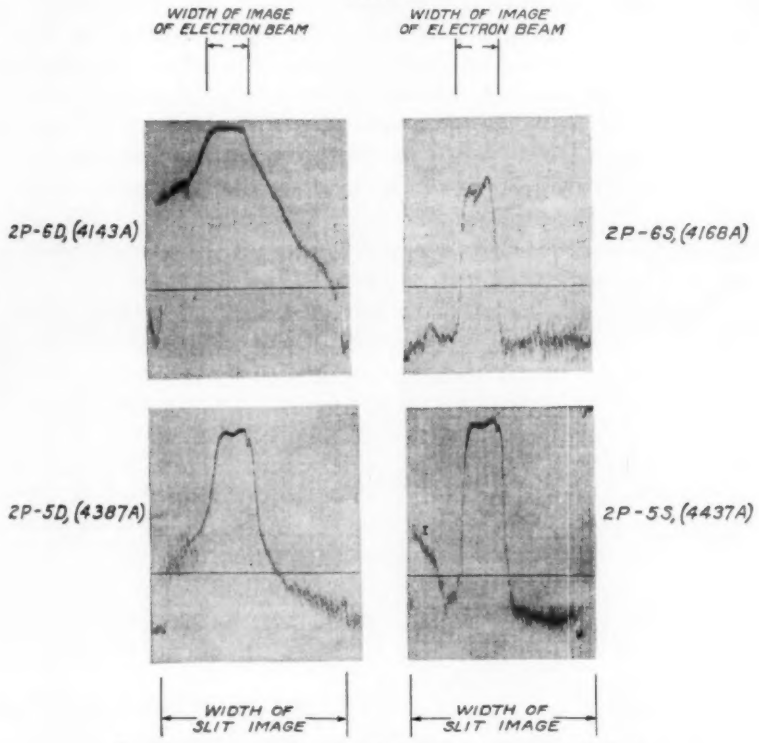
of absorption obtained by McCurdy,[7] who measured the absorption by an absorption cell containing helium in which a weak discharge was set up in order to increase the amount of absorption. The degree of absorption obtained was determined by the width of the reversal of the spectrum lines. McCurdy's results were obtained for a helium pressure of 4 mm. In the present work it is noticed that the 2S – NP series shows absorption up to the fifth term, 2S – 6P (3447A). Paschen showed that the first term 2S – 2P was absorbed while McCurdy found absorption to the fourth term 2S – 5P (3613A). The lengthening of the lines of this series must be considerably enhanced by absorption of also the radiation IS – NP. For the principal series of the triplet system 2s – Np Paschen showed that the first term 2s – 2p (10830A) was absorbed, while McCurdy found absorption up to the third term 3187, 2s – 4p, while here absorption has been found up to the seventh term of this series, 2s – 8p (2723A). McCurdy has found that the 2P – ND series is absorbed only to the second term, whereas in the present work absorption was found up to the fifth term 2P – 7D (4009A), as shown in Table I. Similar to the effect observed by McCurdy no absorption was found for the 2P – NS series. McCurdy finds absorption for the first four members of the 2p – Nd series while Table I shows absorption to the line, 2p – 12d (3512A), but no absorption for the 2p – Ns series.

The present results are in fair agreement with McCurdy's but extend to the higher series members not considered by him. The chief differences obtained are for the lines 4387, 2P – 5D; 3964, 2S – 4P; and 3613, 2S – 5P, in which cases the present work indicates strong absorption while McCurdy's results give either no, or very weak, absorption. Absorption of lines IS – 4P and IS – 5P could account for the increased lengthening of these lines 3964 and 3613. However, the two methods agree in general and these discrepancies are not surprising on account of the two radically different methods employed for measuring the absorption. The recent work of Levy [9] on the anomalous dispersion in excited helium gives results in agreement with the relative values found above, namely that the absorption will be less for the sharp series than for the diffuse series holding true for

both the singlet and triplet systems, also in accordance with the experiments of Takamine and suga.[10]

Figure 2 shows densitometer records taken along the length of the spectrum lines. At the top of the figure is indicated the width of the image of the electron beam, while beneath the record is given the width of the image of the slit of the

FIG. 2.



Densitometer records taken lengthwise of spectrum lines of helium.

spectrograph which limits the length of these lines. It is easily seen that the length of the lines 2P – 6S and 2P – 5S equal nearly the width of the image of the beam while the other two lines 2P – 6D and 2P – 5D are much longer and their lengths are terminated by the length of the slit, which shows that absorption is greater for the diffuse series lines than for the sharp series. The smaller maximum indicated at

I for the record of line 4437 was caused by a fogging of the plate due to scattered light from the filament and is independent of the absorption phenomena concerned here.

The method utilized here for the measurement of absorption involves first the absorption of light by the excited atoms surrounding the electron beam, then the subsequent emission of light of the same frequency, which produces the elongated line in the spectrograph. This method will be subject to errors when transitions occur from upper states to lower levels other than the one originally considered. For example if an electron were excited to the 12d state by absorption of the line 2p − 12d, then instead of returning directly to the 2p state it should first jump to the 3p state then finally go to the 2s level, this process would produce lengthening of the line 2s − 3p, indicating incorrectly absorption for this line, whereas the actual line absorbed would not show any lengthening and consequently not be recorded as absorbed.

The importance of processes of this kind depends upon the relative values of the probability of transitions from the upper levels. In general, for the case of hydrogen the transitions which involve the greatest energy change are the most likely to occur, so that we should expect for helium that the above errors would be of a secondary importance although not necessarily small. In fact it may account for the disagreement found with McCurdy's results, since McCurdy measured more truly the real absorption free from the above errors. Since values of the transition probabilities for helium have not yet been obtained which can be used for the present case, it is impossible to compute accurately the effect produced by the errors mentioned above.

Recombination of ions and electrons in the vicinity of the electron beam would give rise to excitation of the higher quantum states and tend to enhance the lengthening of lines coming from higher excited states. If this action occurred to any great extent continuous spectra should be present, and the lack of its appearance indicates that recombinations were not occurring, also the transverse electric field sweeps out the ions from the vicinity of the electron beam which greatly diminishes the probability of recombination with electrons from taking place. Therefore errors due to recombination are evidently not present.

SUMMARY.

(1) The present work substantiates the results of previous experiments which show that absorption can take place in excited helium not only from the 2S and 2s metastable levels but also from the non-metastable 2P and 2p states. The absorption for higher series members than has hitherto been reported is also proved.

(2) The previous determined fact that the diffuse series lines are more easily absorbed than the sharp series has now been found to hold for higher terms of these series.

(3) The region in close vicinity to an electron beam in helium contains a relatively large number of excited atoms in both metastable and non-metastable states, capable of producing absorption.

THE PROBABILITY OF ELECTRON EXCITATION OF THE SHARP SERIES OF ORTHOHELIUM.

The peculiar distortion which was found to be common for all of the lines of the sharp series 2p − Ns, indicates that there is a particular velocity range of electrons which excites most efficiently the lines of this series. It would therefore be expected that the maximum of the electron excitation function is approximately the same for all of the lines of this series examined. Also since the intensity of the lines of this series decreases for increasing values of N, it is concluded that the relative efficiency decreases progressively for the higher members of the series. These results are in good agreement with those obtained by Hanle [11] who has studied the excitation of the lines 2p − 4s (4713A), 2p − 5s (4121A), 2p − 6s (3867A) and found the shape of the intensity—voltage curves very nearly alike and also the position of the maxima occurring at about 30 volts for these lines. Hanle also found that the intensity became less for the higher series lines. Elenbaas [12] has also obtained intensity—voltage curves for the two lines 4713A and 4121A which agree approximately with Hanle's curves for these lines.

The present work shows that these same relationships as regards the position of maxima and relative intensity will also hold for the two next higher lines of this series 2p − 7s (3732A) and 2p − 8s (3652A).

NOTE: Lees (*Proc. Roy. Soc.*, *A137*, 173 (1932)) and Lees and Skinner (ibid., *A137*, 186 (1932)) have just reported results on the lengthening or spreading of helium lines which agree quite well with the present results. They explained the spread of the 2p — Nd lines by atomic collisions with excited atoms in the NP states. This conclusion was obtained after disregarding the possibility of absorption because their intensity-current measurements showed linearity relationships to exist for these lines, implying that single electron collisions were responsible for the radiation produced. Although the lines 2p — Nd were linear with respect to electron current, one cannot exclude the process of absorption until the experiments prove that the population of the 2p states outside of the beam is a linear function of the electron current. This would of course necessitate intensity-current measurements of the line 2s — 2p (λ = 10830) in a region outside of the electron beam.

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4. Ref. cit.
5. Ref. cit.
6. Cf. for instance, J. FRANK. INST., **210**, 427 (1930); also *Phys. Rev.*, **38**, 1664 (1931).
7. Ref. cit.
8. *Phys. Rev.*, **38**, 1664 (1931).
9. Ref. cit.
10. Ref. cit.
11. W. Hanle, *Zeit. f. Physik*, **56**, 94 (1929); see also W. Michels, *Phys. Rev.*, 36, 1362 (1930).
12. W. Elenbaas, *Zeit. f. Phys.*, **59**, 289 (1930).

IONIZATION OF THE ATMOSPHERE AND ITS BIOLOGICAL EFFECTS.

BY

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PART I.

Air conditioning at the present time consists in the attempt to control temperature and moisture content of the air inside buildings, as well as the elimination of dust and unpleasant or harmful gases or vapors. Another atmospheric factor which may possibly have considerable bearing on human well being has been largely overlooked so far. This factor is the electrical condition of the atmosphere. Evidence has been acquired recently which indicates that this factor may be important, and, therefore, it may be desirable to attempt to control it artificially. Before discussing the evidence and the methods of producing and controlling atmospheric electricity, it is necessary to describe the normal condition of the atmosphere and the various methods of investigating it experimentally.

The first investigation of the electrical conductivity of the atmosphere was made by Coulomb in 1785. Coulomb studied the loss of charge by a metallic conductor in air. Previous to this time it was thought that this was entirely due to faulty insulation and that a perfectly insulated charged body could maintain its charge indefinitely. Coulomb showed that the loss was not entirely due to insulation leakage, but in part also due to conduction through the atmosphere, although his theory of the nature of this conduction was erroneous.

About a century later, in 1887, Linns also investigated the conductivity of the atmosphere and found that it was greatest in fine weather, and, furthermore, that it showed a seasonal variation.

The true nature of this conductivity, however, was not discovered until 1900 by Elster and Geitel [1] as a result of a

[1] Elster and Geitel, *Phys. Zeit.*, 1, 11 (1899).

study of the effects produced in air by X-rays and Becquerel rays.

In contrast to the lack of knowledge regarding the conductivity of the air, the potential gradient of the atmosphere has been known for nearly two hundred years. In 1752 LeMonnier showed that there is everywhere a permanent potential difference between the earth and the air. This is ordinarily approximately 100 to 300 volts per meter at the earth's surface; that is, the air is generally at a positive potential of some hundreds of volts with respect to the surface of the earth. It is subject to hourly and daily fluctuation and varies from place to place. It is somewhat higher in winter than in summer. This gradient decreases with increasing altitude. Typical values at different elevations are given in Table I.

TABLE I.[2]

Elevation in Meters.	Gradient in Volts/M.
0	100
1000	25
3000	10
6000	a few

Under the influence of this field, a current of about 2×10^{-16} amps./cm.^{2} is constantly flowing towards the earth. Integrated over the entire surface of the earth, this corresponds to a current of 1000 amperes.

The resistance of the air is extremely high. The conductivity of metallic copper is 3.5×10^{21} times as high as that of atmospheric air, while even that of a 5 per cent. NaCl solution is 10^{14} times as high.

In addition to the current which flows under the influence of the atmosphere's potential gradient, there are also localized convection currents due to the motion of charged masses, such as fog, rain, snow or dust, and the like, and also the large currents due to lightning discharges.

The conductivity of the air is due to the presence at all times of large numbers of ions or charged particles. In general, the number carrying positive charges is slightly larger than the number carrying negative charges. The number of ions is also subject to great fluctuations from

[2] Gerdien, *Phys. Zeit.*, **6**, 647 (1905).

hour to hour and from place to place. In any one place it shows a daily as well as a seasonal variation. It is usually largest when the air is clear. It is larger in summer than in winter; larger during the day than at night, and when the temperature is high than when it is low. Unlike the potential gradient, the number of ions increases with increasing elevation. At very high altitudes the number becomes very large and the conductivity becomes very great. This highly conducting layer is the Heaviside layer which is responsible for many phenomena observed in the long distance transmission of radio waves.

In recent years much information has been gained as to the nature of the ions. It is now fairly certain that they start out as atoms or molecules from which an electron has been removed, thus forming a positive ion of molecular size and a negative ion consisting of a single electron. At atmospheric pressure, however, they do not continue long in this condition, but each ion forms about itself a cluster of molecules held together by electrostatic forces. The size of the cluster depends, to some extent, on its age. These clusters probably consist of about ten molecules. These aggregates constitute the large part of the ions in air and are responsible for most of the conductivity. They are called light ions to distinguish them from the heavy ions formed by the attachment of a positive or negative ions to dust or water particles in the air. These heavy ions are called Langevin ions after their discoverer.

Since the dimensions or masses of the ions cannot be measured by any direct means, it is customary to describe them in terms of their velocities. If we consider an ion in an electrostatic field, it will acquire a characteristic velocity which depends upon the field strength and upon the nature of the ion. The velocity in cm./sec., when the ion is placed in a field of 1 v./cm., is called the mobility. The mobility of the light ions is 1–2 cm./sec./v./cm., while the mobility of the heavy ions is 0.01–0.0005 cm./sec./v./cm. Measurements of ionic mobilities are of great importance because it is only through them that we can gain information as to the nature of the ions. These measurements are particularly difficult to make in atmospheric air due to the very weak ionization.

The number of ions present in the air at any time is the result of equilibrium between the processes which are tending to produce ions and those which are tending to destroy ions. These processes will be discussed later in detail.

Much information as to the nature of the ions in air can be gained from relatively simple electrical measurements. The earliest measurements made were those of conductivity. The rate of loss of charge of a conductor is proportional to the conductivity of the surrounding atmosphere. This was shown by Coulomb to be

$$-\frac{dQ}{dt} = 4\pi Q\lambda \text{ where } \lambda = \text{conductivity.}$$

Since $\frac{dQ}{dt} = C\frac{dV}{dt}$, it is possible to measure the voltage of a condenser at frequent intervals, and from the rate of decrease to calculate λ. One objection to this method is that the measurement itself alters the ionic distribution in the neighborhood of the conductor and so fails to give a correct measure of the conductivity.

This difficulty is overcome by the aspiration method of Gerdien.[3] In Gerdien's apparatus, which is shown in Fig. 1, air is drawn between the electrodes of a cylindrical condenser. A known potential is applied between these electrodes, and from the rate of loss of charge and the volume of air drawn through, the conductivity can be calculated. Let us consider, first, the current between a pair of plane parallel electrodes 1 cm.^{2} in cross section and 1 cm. apart with a potential E applied between them. The current (i) flowing between them will be proportional to the field strength (E), to the number of ions of each sign per unit volume (n), their mobility (u) and to the charge carried by each (e).

$$i = E(n_+u_+e + n_-v_-e)$$

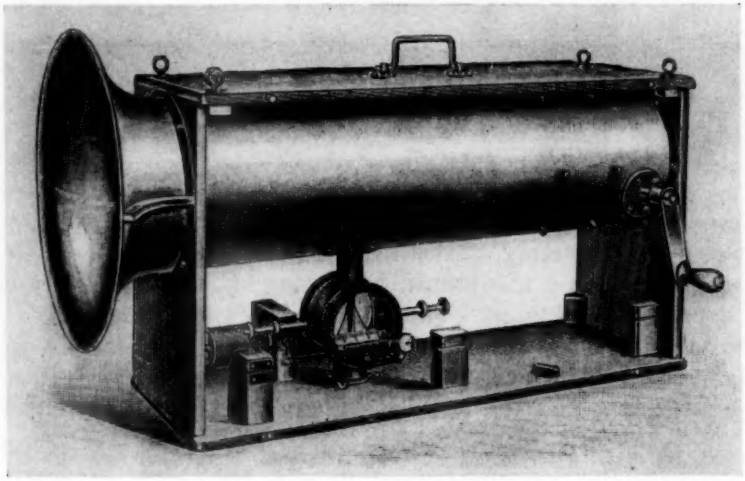
the conductivity $\frac{i}{E} = \Delta = \lambda_+ + \lambda_-$. The total conductivity then is made up of two terms, the positive and negative polar conductivities, due to the positive and negative ions respectively.

[3] Gerdien, *Phys. Zeit.*, **6**, 800 (1905).

In the case of a stream of air containing ions passing through a cylindrical condenser, as in Gerdien's apparatus, ions will be drawn to the electrodes by the applied field, and, accordingly, the charge collected will be a measure of the number of ions per unit volume and their mobility, that is, the conductivity. In using the apparatus, air is drawn through the collector for a time interval, t, and the potential of the collector is observed at the beginning and end of this time interval, then

$$\lambda_{-} = \frac{K \log V_1/V_2}{t}.$$

FIG. 1.



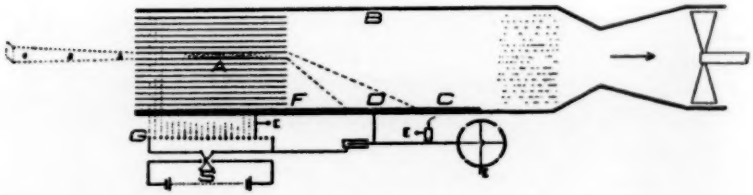
Since both mobility and ion content enter into the expression for conductivity as a product, this measurement does not suffice to determine either. The ion content can be determined, however, by a slightly different method of using the same apparatus suggested by Ebert.[4] If a high enough potential is applied between the electrodes to collect all the ions which enter the condenser, the charge collected in a given time divided by the volume of air drawn through the condenser will give the number of ions per unit volume of air.

[4] Ebert, *Phys. Zeit.*, **2**, 662, 1901.

Since the conductivity and ion content are both known, the mobility can be calculated from their ratio.

There are several more direct methods of determining mobility, however. The method used by Erikson [5] is shown in Fig. 2. Air is drawn through the tube past a source of radio active material at A which ionizes some of the molecules. In the absence of any electric field, these would continue through the tube in a straight line. A field is applied between the electrodes C and B, however, such that a positive ion will be deflected towards B. A narrow strip, D, can be moved along the tube practically in the plane of C and is

FIG. 2.



connected to an electrometer so that the current to it can be measured separately. It is moved along the tube until the current to it is a maximum, indicating that it is directly in the path of the ions. The path taken by the ions is the resultant of their motion due to the velocity, s, of the air stream and the velocity imparted to them by the field. If the mobility is u and the applied potential is V, then the field strength is $\frac{V}{h}$ and their velocity across the tube due to the field is $\frac{uV}{h}$.

$$\frac{h}{d} = \frac{\frac{uV}{h}}{s}$$

and $u = \frac{sh}{dV}$.

This method, as well as most of the other methods de-

[5] Erikson, *Phys. Rev.*, **18**, 100 (1921).

scribed, assumes only one or more discrete ion mobilities and does not take into account the distribution of mobilities.

Another method is based upon the variation of current with voltage when ions pass through a cylindrical condenser.

If we consider the case of a cylinder condenser with an outer electrode of radius, b, and an inner electrode of radius, a, and an applied voltage, V, the field strength, F, at a distance, r, from the axis will be

$$F = \frac{V}{r \ln \frac{b}{a}}.$$

The velocity of an ion in the direction of the field will be the product of its mobility u and the field strength.

$$uF = \frac{uv}{r \ln \frac{b}{a}}.$$

An ion entering the condenser at a distance r from the axis will reach the collector at a distance x from the end where x is determined by the relation between the velocity due to the field and that due to the velocity of the air stream W.

$$\frac{dx}{dr} = \frac{W}{uF} = \frac{rW \ln \frac{b}{a}}{uV}.$$

Integrating this

$$x = \int_a^r \frac{W}{uV} \ln \frac{b}{a} r dr = \frac{W}{uV} \ln \frac{b}{a} \frac{r^2}{2} \Big]_a^r$$

$$= \frac{W}{2uV} \ln \frac{b}{a} (r^2 - a^2);$$

a^2 can be neglected in comparison with r^2.

$$\therefore \quad u = \frac{Wr^2}{2xV} nl \frac{b}{a}.$$

The time required for an ion to travel from r to the collector is

$$t = \int_a^r \frac{dr}{uF} = \int_a^r \frac{r \ln \frac{b}{a} dr}{2uV} (r^2 - a^2).$$

All ions which enter the collector at a distance from the axis less than r are caught. That is, all ions within the cylinder of volume $\pi(r^2 - a^2)$. The ratio of the number of ions caught to the total number entering the condenser is the ratio of this volume to the total volume of the condenser, or

$$q = \frac{\pi(r^2 - a^2)}{\pi(b^2 - a^2)} = \frac{2uVt}{(b^2 - a^2)ln\frac{b}{a}},$$

but q = the ratio of the current, i, to the collecting electrode to Qne the total charge passing through the tube, or

$$q = \frac{i}{Qne} = \frac{2uVt}{(b^2 - a^2)ln\frac{b}{a}},$$

where Q = total volume of air passing through collector

$$\therefore \quad i = \frac{2uVQne}{(b^2 - a^2)ln\frac{b}{a}}.$$

Accordingly, if ions of only one value of mobility are passing through the tube, the current to the collector will be a linear function of the applied voltage until a high enough voltage is reached to collect all the ions, when saturation will be attained. The slope of the curve will be proportional to the mobility and the saturation voltage will be inversely proportional to the mobility. If ions of several different discrete values of mobility are present, the curve will show several straight portions corresponding to the different values of mobility. The breaks in the curve indicate the points at which all of the ions of any one value of mobility are caught and the value of u can be calculated from the above equation.

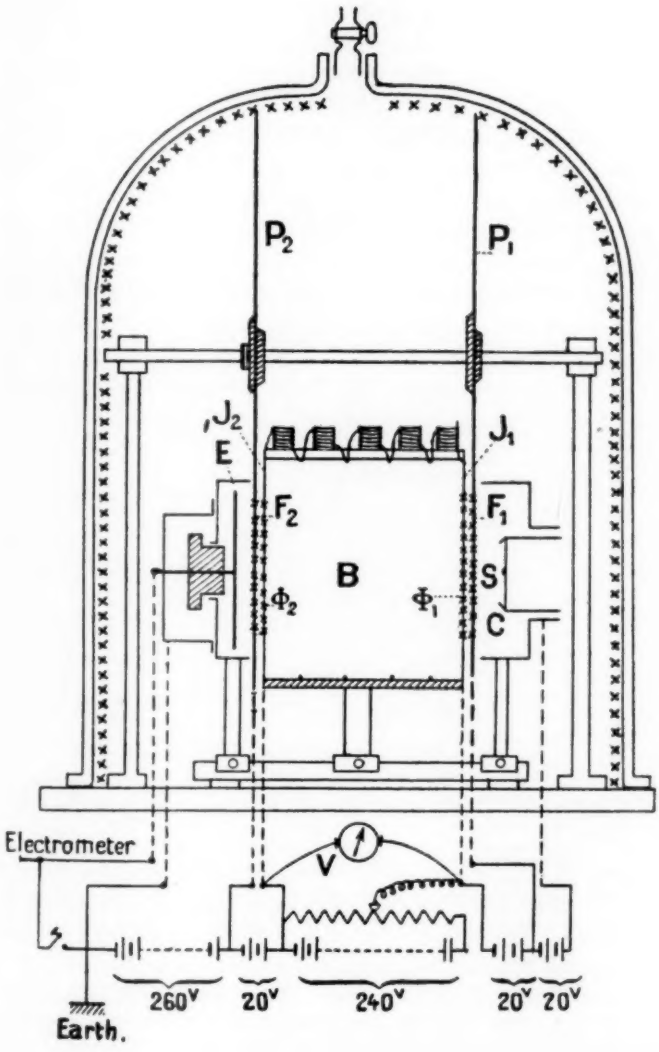
In general, the results of a large number of observers indicate that the light ions in air have mobilities of 1 to 2 cm./sec./v./cm., depending, somewhat, on the moisture content of the air.

Zeleny [6] gives the following values for the mobility of ions in a number of different gases.

[6] Zeleny, *Phil. Trans. A.*, **195**, 193, 1900.

Gas.	M_+.	M_-.
Dry air	1.36	1.87
Dry hydrogen	6.70	7.95
Dry oxygen	1.36	1.80
Dry carbon dioxide	0.76	0.81

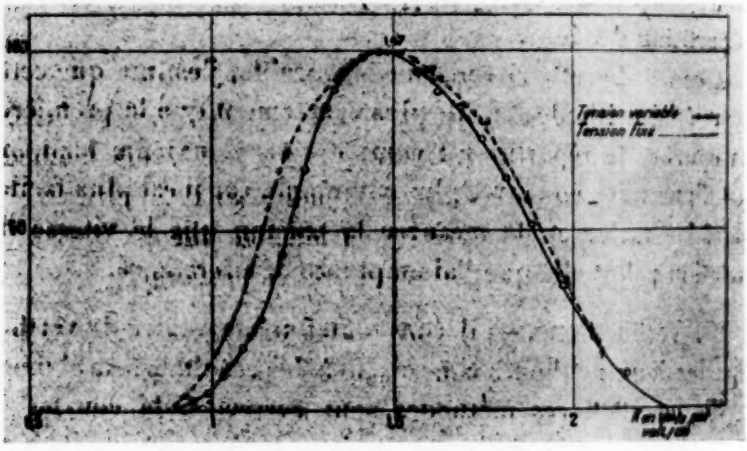
FIG. 3.



A method used by Laporte [7] permits the determination of the distribution of mobilities with a high degree of accuracy. In Laporte's apparatus, Fig. 3, ions are formed by the action of radioactive matter in the chamber c and are drawn over to the electrode E. To reach E they must pass through the slits in the two discs P_1 and P_2 which are rotated on a common axis. If the slits were infinitely narrow, an ion would just be able to reach E if the angular distance between the slits corresponded to the time required for an ion to traverse the distance between the two plates. This condition is attained either by varying the speed of rotation or the applied voltage. In practice, of course, the slits are of finite width and the ions show a distribution of mobilities about a mean value.

Laporte obtained curves for the distribution of mobilities, of which Fig. 4 is typical. This particular curve is for the mobility of positive ions in air saturated with water vapor.

FIG. 4 (top).



A number of very interesting conclusions are arrived at from the measurements made by Laporte. He found that the mobility distribution curves for positive ions in air, oxygen and nitrogen were practically identical. On the other hand, in the case of negative ions, the curves for air and oxygen were

[7] Laporte, *Ann. de Physique*, 8, 466 (1927).

identical, while the curve for nitrogen showed a decidedly lower mobility. He interprets these results as indicating that the negative ions in air and oxygen are the same, that is, they are oxygen ions. In other words, negative nitrogen ions are not readily formed by the attachment of an electron to a neutral nitrogen molecule so that in air all of the negative ions are oxygen. This is due to the fact that the electron affinity of oxygen is much greater than that of nitrogen.

The effect of moisture is to increase slightly the mobility of the negative ions in the case of air. The effect of humidity is not the same for all gases, but depends upon the nature of the gas. Laporte explains this by the assumption that the ion cluster consists of an ionic nucleus to which are attached a number of molecules of water and a number of neutral gas molecules. The relative numbers will depend upon the humidity of the gas and upon its electron affinity. In the case of a gas whose molecular weight is greater than that of water, the effect of substituting water molecules for gas molecules in the cluster would be to increase the mobility.

On the other hand, if the gas molecules are lighter than water molecules (as in the case of H_2), the effect of water vapor would be to decrease the mobility. If the gas molecules have no affinity for ions, then increasing humidity would tend to lower the mobility. Sufficiently precise measurements are not yet available for a satisfactory verification of this hypothesis.

Several other methods are reviewed by Przibram in "Handbuch der Physik."

The effect of pressure is to decrease the mobility. Over a very wide range it varies inversely as the pressure. The effect of increasing temperature is an increase in mobility.

Another theory has been proposed by Wellish [8] instead of the ionic cluster theory to explain the low mobility of ions. Wellish accounts for the low mobility by assuming a lowering of the mean free path due to the attractive forces of the electrostatic charges carried by the ions.

The difference in mobility between the positive and negative ions has a very interesting consequence.[9] If we

[8] Wellish, *Phil. Trans. A.*, **209**, 249 (1909).

[9] Ebert, *Jahrbuch der Radioaktivitat*, **3**, 63 (1906).

consider the case of an ion carrying a charge, e, at a distance, a, from a conducting surface, the attractive force acting upon it due to electrical image forces will be

$$f = \frac{e^2}{4a^2}.$$

The field strength

$$F = \frac{f}{e} = \frac{e}{4a^2}.$$

Due to this field, the ion will acquire a velocity $\frac{ue}{4a^2}$ in addition to its velocity due to thermal agitation. The time required for it to reach the wall under the influence of this force is

$$t = \frac{4a^2}{ue}, \qquad da = \frac{4a^3}{900ue} \text{seconds.}$$

For a positive ion at a distance of 1 mm. from a conducting surface, this time would be 1 hour and 44 minutes. At a distance of 0.054 mm. ions would reach the wall in 1 sec., while from a distance of 10^{-3} mm., the time required would be 6.2×10^{-6} sec. Accordingly, although the effect of ion adsorption by conducting surfaces is comparatively small for large volumes of gas, it may become very large where gas is caused to stream through very narrow passages, that is, where the wall surface is large in comparison with the volume of air drawn through as in the case of cracks and capillaries.

Thus, near the walls ions are removed by adsorption. This lowers the concentration in this region, and, due to the concentration gradient, diffusion takes place. Since the mobility of the negative ions is greater than that for positive ions (and also their rate of diffusion), more negative ions will be adsorbed by the wall in a given time than positive ions so that air which has passed through narrow passages should contain an excess of positive ions. Zeleny [10] has shown experimentally that this is the case. This phenomenon probably plays an important rôle in the production of the excess of positive charge in the atmosphere. Under some

[10] Zeleny, *Phys. Zeit.*, **4**, 667 (1903).

conditions, the area of conducting surface in the air may become quite large, as, for example, when much dust or fog is present so that negative ions may be absorbed by particles which are eventually removed by falling to earth under the influence of gravity. A much greater effect is probably due to the respiration of the soil. Approximately 50 per cent. of the volume of the soil is air. This air becomes highly ionized by the small amount of radioactive matter which is present in the soil. Due to changes in temperature and barometric pressure and the action of winds, this ionized air is drawn out of the pores of the soil. In its passage through the capillaries there is a selective adsorption of negative ions which leaves the escaping air with a slight excess of positive charge.

So far the discussion has been limited to the behavior of light ions. The mobilities of the heavy or Langevin ions, which are really microscopic and submicroscopic particles, are of a different order of magnitude and do not show any discrete values.

The forces which tend to form ions in the atmosphere are varied in nature. A small number may be formed by the photoelectric effect. At the surface of the earth this effect must be negligibly small since none of the materials of the earth's crust are photoelectrically sensitive excepting in the extreme ultraviolet, and this radiation is all absorbed in the upper region of the atmosphere. There may be some ions formed due to the photoelectric activity of ice needles in the very highest clouds.

There is also the possibility of ionization by ultraviolet radiation in the upper layers of the atmosphere.

Some ionization is produced by cosmic radiation. As yet, there are no satisfactory quantitative data available with regard to this.

The splashing of water to form spray may be responsible for some of the ionization near bodies of water. In general, the spraying of pure water produces negative ions in the surrounding air. A small concentration of salts in the water, however, reverses the effect. Accordingly the spray produced by sea water charges the air positively. Probably the largest single factor in producing ions is the radioactive

matter present in the soil. While the quantity of radioactive matter is small, it is very widely distributed and so produces ions near the surface of the earth and in the pores of the soil from which it is withdrawn by the so-called respiration of the soil. The decomposition of the radioactive material in the soil produces radioactive decomposition products which are gases so that there is a very wide distribution of ionizing material in the atmosphere as well as in the earth's crust. Although the quantitative effect of each of these factors is not known, it is fairly certain that they all play some part in maintaining the ion content of the atmosphere. In addition, there may be some other unknown agencies operating. Hess [11] has shown that about half of the ionization of the atmosphere may be accounted for by the radioactive material known to be in the air and in the earth's crust.

The forces leading to the destruction of ions are more easily evaluated. One of these has already been mentioned, namely, the adsorption on conducting surfaces.

Another factor is recombination of positive and negative ions and the consequent neutralization of charge.

A third factor is fixation of charges by adsorption of ions on solid or liquid particles. This is not a true destruction of ions, but since their mobility is lowered by adsorption on relatively large particles, they are no longer effective in producing conductivity.

The coefficient of recombination has been determined experimentally by a number of different methods.

The method used by Langevin [12] was to ionize the air in the space between two condenser plates by X-rays. The radiation was then stopped and the ion content of the space measured by applying a field between the plates and measuring the charge collected. The process was then repeated excepting that the charge was measured after a time, t, had elapsed after the ionizing radiation had been stopped. The charge measured this time was less than initially because some of the ions had been lost by recombination. The rate of recombination is proportional to the number of positive and

[11] Hess, "Electrical Conductivity of the Atmosphere," p. 168.

[12] Langevin, *Ann. Chem. and Phys.*, **28**, 433 (1903).

negative ions present, or if they are present in equal numbers to n^2. Accordingly the rate of decrease of the ion content is

$$\frac{dn}{dt} = -\alpha n^2.$$

Integrating this

$$\frac{1}{n} - \frac{1}{n_0} = \alpha t.$$

From the two observed values of n and n_0, and the time interval between the two observations, α can be calculated.

Another method used for the determination of α by Zeleny [13] consists in allowing a gas to stream through a tube over a source of radioactive material, where ions are formed, and then past electrodes, by means of which the ion content of the gas can be determined. The rate of flow of the gas gives the time required to pass from one electrode to the other. The ion content of the gas is determined at each electrode. Then, as in the previous case,

$$\frac{dn}{dt} = -\alpha n^2$$

and

$$\frac{1}{n} - \frac{1}{n_0} = \alpha t.$$

Values of α determined by different investigators are in very good agreement. An average value is $\alpha = 1.3 \times 10^{-6}$.

PART II.

We will now turn from the consideration of the electrical condition of the atmosphere to the biological effects of atmospheric electricity. This field is relatively new. It is rapidly being explored by Professor Dessauer and his colleagues at the Institute für Physikalische Grundlagen der Medizin at the University of Frankfurt, and by Professor Yaglou at the Harvard School of Public Health, as well as by a number of other workers. There is no simple direct relation between the magnitude of the ion content of air and the reactions of people, although there are a few scattered

[13]

observations which indicate that the ion content of the air exerts some influence upon human health. For example, in 1902 Caspari [14] measured the ionization at certain points in the mountains and ascribed mountain sickness to excessively high values of the ion content. There seems to be some ground for this theory in view of the fact that climbers have experienced mountain sickness in certain definite localities and have been free from it at slightly higher or lower elevations. In 1903 Sokoloff correlated his rheumatism with exceptionally high values of the ion content of the air which he observed in the Caucasus.

A consideration of the effects on people of various types of climate, such as mountain and sea level; the effects produced by radioactive springs; phenomena, such as mountain and Föhn sickness, and the dependence of rheumatic and gouty diseases upon the weather lead Professor Dessauer to the conclusion there is present in the atmosphere at least one other physical factor in addition to such other factors as pressure, temperature, radiation and humidity. He, as well as others, has suggested that this factor is the ion content of the air.

Accordingly, he devised a method for producing ions of one sign only in sufficient quantity to test their biological action. The various methods for doing this will be discussed in greater detail in Part III. At this point it is sufficient to state that the method used produced air with an ion content of 10^6 ions/cc. These ions were intermediate between light ions and Langevin ions. They consisted of aggregates of about 50,000 molecules of MgO so that they can be considered as submicroscopic dust particles. Tests showed that the MgO was pharmacologically inert so that any results observed must be ascribed to the charges.

Although an ion content of 10^6 ions/cc. appears large, it must be remembered that the number of molecules of gas per cc. at atmospheric pressure is 2.7×10^{19} therefore the percentage of the molecules ionized is extremely small.

A large number of experiments were carried out by allowing patients to inhale the ionized air in a small test chamber. It was found that with ions of the type mentioned

[14] *Phys. Zeit.*, p. 521 (1902).

having mobilities lying between 0.0007 and 0.009 cm./sec./v./cm. approximately 15 to 40 per cent. of the inhaled ions were retained in the lungs. When heavier ions were used, the absorption in the lungs was much less. In the case of lighter ions, the absorption in the passages of the nose and throat was so great that only a relatively small proportion of the ions actually reached the lungs.

Observations were made of blood pressure; rate of respiration; as well as subjective reactions. In most cases, positive ions produced feelings of fatigue, dizziness, headaches, roaring in the ears, nausea, and the like, in a greater or lesser degree. Negative ions in most cases produced a feeling of exhilaration. There were, however, some exceptions with each sign of ion.

The measurements of blood pressure of healthy individuals showed that after inhaling air with a high concentration (10^6 ions/cc.), of negative ions from one half hour to one hour, the blood pressure is lowered from 5 to 15 mm. Soon after stopping the inhalation, the pressure returns to its normal value. The effect of positive ions is to increase the blood pressure slightly, but the effect is less marked. The positive ions, however, tend to produce headaches and discomfort.

The effect of ions on the rate of respiration is shown in Fig. 5. Positive ions greatly increase the rate of respiration, while in the case of negative ions, patients breathe more quietly and there are frequent pauses in respiration. There also appears to be an increase in oxygen consumption under the influence of positive ions.

Dessauer's most striking results, however, were the therapeutic effects of ionized air upon persons suffering from a group of diseases which included high blood pressure, rheumatism, gout, neuritis and neuralgia, acute and chronic bronchitis, cardial and bronchial asthma and heart and arterial diseases.

He found that in the case of persons suffering from high blood pressure, the inhalation of negative ions at frequent intervals over a period of some weeks produced a decrease in blood pressure which persisted for a longer time, and a general improvement in condition. In a study of 200 cases of patients with high blood pressure, there was a permanent improvement in 80 per cent. of the cases.

In cases of rheumatism the inhaling of ionized air resulted in increased pains, swelling of joints, and a rise in temperature followed later by an improvement in the condition.

In general, it may be stated that the inhalation of negative ions affects the condition in much the same way as mountain

FIG. 5*a*.

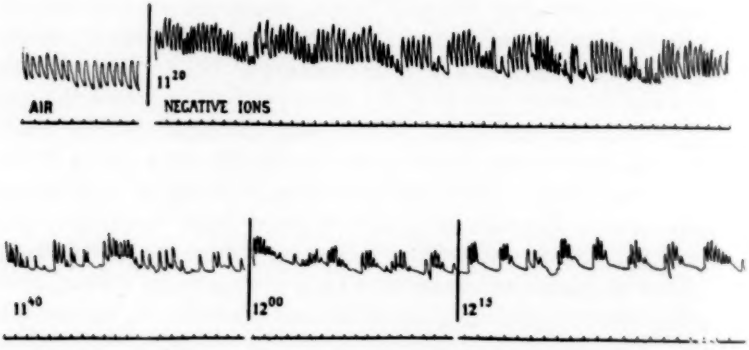
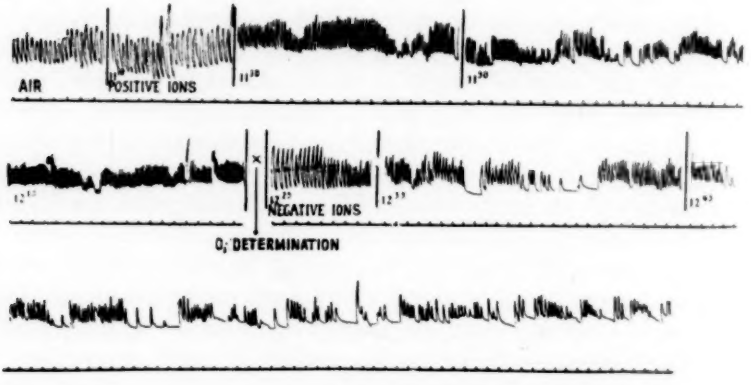


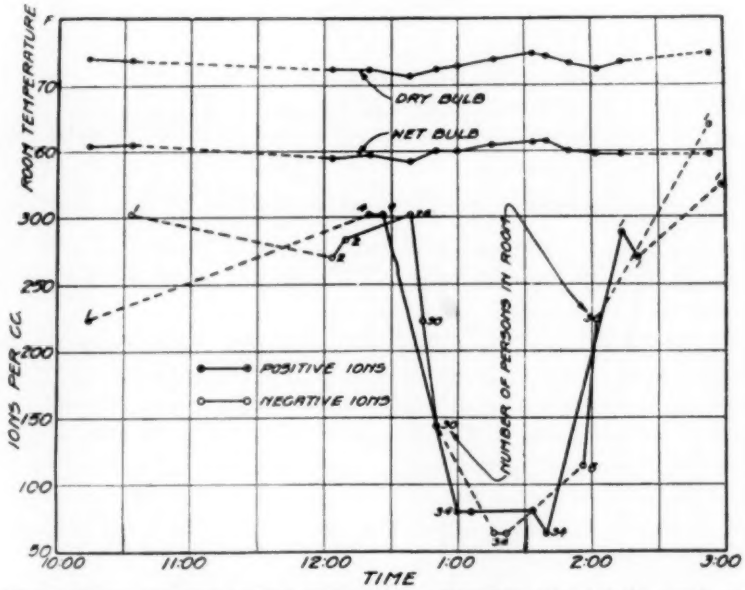
FIG. 5*b*.



climate. Falling barometric pressure, which generally affects the condition adversely, tends to withdraw air from the soil. This air usually has a high positive ion content due to adsorption phenomena. The Föhn wind experienced in the Alps, which also produces discomfort, also has a high positive ion content.

The problem of ventilating, however, is concerned with much lower ion concentrations than those used in the investigation of therapeutic effects. An interesting investigation has been made by Professor Yaglou on the ion content in rooms. In general, it was found that in unoccupied rooms the ion content of the air was not very different from that out of doors. In occupied rooms, however, the ion content shows a very marked decrease. This is shown very strikingly by Fig. 6 taken from Yaglou's paper. "The loss of ions in

FIG. 6.



Influence of room occupancy on ionic content. Room dimensions 30 ft. × 33 ft. × 10 ft. 6 in. Number of occupants, 34. Good window—gravity ventilation.

these experiments cannot be accounted for by respiratory processes alone, even if it is assumed that the expired air is completely devoid of ions. This is because the volume of air breathed by the occupants (0.28 to 0.42 c.f.m. per person) is very small in proportion to the cubical content of the room (300 a ft. air space per occupant in the class room)."

Mechanical ventilation was found to reduce the ion content up to as much as 30 per cent., probably due to adsorption of

ions on metal surfaces. Washing the air and humidifying or dehumidifying by means of water sprays deprived the air of all small ions and produced a great number of large negative ions.

The present problem of the ventilating engineer is to ascertain, first of all, the biological effects of various ion concentrations and then to devise suitable means of controlling the ion content.

PART III.

Various methods have been suggested for the production of ions. Dessauer gives the following list:

X-rays
Ultra-violet
High voltage brush discharge between needle points 2 cm. apart
High frequency
Flames
Incandescent alkalis and metals.

Dessauer states that with X-rays a concentration of 5×10^3 ions/cc. could be obtained. This is not sufficiently high, however, to be a very practical method.

At six inches from a 75 watt mercury arc in quartz, the writer obtained a concentration of 76,000 ions/cc. Due to the rapid rate of recombination, however, at a distance of thirty inches from the lamp, the concentration fell to the normal value for the room. Furthermore, this method is objectionable due to the production of ozone and oxides of nitrogen. The same objection applies to the high voltage brush discharge.

The method used by Dessauer consisted in heating a block of pure MgO by passing a current through a platinum filament wound around it and blowing an air stream over it. The block measured $2 \times 3 \times 0.8$ cm., and was wound with 0.2 mm. wire. By heating the wire to a temperature of 1200° C., the block was heated to 950° C. By means of a system of grids, to be described later, this device was made to yield air with an ion content of 10^6 ions/cc. at the rate of 1 L/sec. These ions were found to be charged particles of MgO having mobilities lying between 0.007 and 0.009 cm./sec.

The mass of the negative ions was determined to be 7.5 $\times 10^{-18}$ grams and of the positive ions 3.8 $\times 10^{-18}$ grams. One of the main drawbacks to the method was the fact that the efficiency of the ion generator fell off about 50 per cent. per hour, and that its life was limited to 12 or 15 hours.

The separation was effected by blowing the ionized air through a grid which was maintained at a high d.-c. potential with respect to the MgO. The degree of separation obtained by Dessauer at various grid potentials is shown in the following Table III where the second column gives the per cent. of negative ions in the air stream after passing the grid.

TABLE III.

Volts.	Neg./Pos. × 100.
0	128
400	61
800	48.5
1600	28.7
2400	20.5
5000	4.1
7000	1.1

The degree of separation is, of course, a function of the velocity of the air stream, and the mobility of the ions and the grid mesh, as well as of the grid potential.

The losses in this method of separation are considerable so that the efficiency is very low. Thus in some measurements made by the writer on light ions using a 40 mesh grid at + 2000 volts and an air speed of about 20 ft. sec., a ratio of positive to negative of 0.222 was obtained, the total number of negative ions, however, was only 5.8 per cent. of those generated.

Dessauer found that ions could be passed through tubes with relatively small losses, as shown by the following table.

TABLE IV.

Loss for Negative Ions in Tube 20 mm. Diameter.

Air velocity cm.^{3}/sec.	1000	1000	40
Tube length (M)	8.25	4.6	4.6
Loss	25%	15%	65%

The loss increases with increasing ion content and is greater for positive than for negative ions.

The writer has developed a very convenient method for the production of light ions. This consists of a brass cylinder 5″ in diameter with a coaxial 1 mil tungsten wire a foot long. A potential of several thousand volts of half wave rectified A.C. is applied to the wire while the brass cylinder is grounded and a stream of air is blown through the cylinder. At a voltage of 7000 volts, which is well below the corona voltage, there is no perceptible odor of ozone and an ion content of 10^7 ions per cc. is obtained with an air flow of 6 liters per second. The ions are of the same sign as the potential of the wire; ions of the opposite sign being present to less than 1 per cent. Ions of both signs are formed in the intense field near the wire which is approximately 320,000 volts/cm. Ions of the opposite sign move out towards the wall. Many of these go to the wall and are lost, but some (particularly the low mobility group) are blown out before reaching the wall. It was found that 69 per cent. of the ions generated had mobilities in excess of 0.48 cm./sec./V./cm. The efficiency of this generator could be increased nearly ten fold by eliminating the brass cylinder and simply using three heavy wires parallel to the central wire arranged on the circumference of a five inch circle. This gave a field of the same intensity at the central wire, but provided a much smaller surface for the adsorption of the positive ions.

A vacuum tube amplifier was used for studying the output of the generator. The collector was a cylinder condenser with an outer electrode consisting of a brass tube 10 in. long and $1\frac{1}{2}$ in. in diameter. The inner electrode was a rod $\frac{3}{8}$″ diameter and 5″ long with tapered ends. The outer cylinder was raised to a positive or negative potential, depending upon whether it was desired to measure positive or negative ions. The inner collector was connected to ground through a resistance of 1.4×10^8.

The drop across the resistance was applied between grid and filament of an FP-54 low grid current amplifier tube. The change in plate current was observed when air was drawn through the collector tube. This gave a measure of the change in the drop across the grid R, and, therefore, the ion current. The mutual conductance of the amplifier was 25×10^{-6} amps. per volt. The grid resistance was

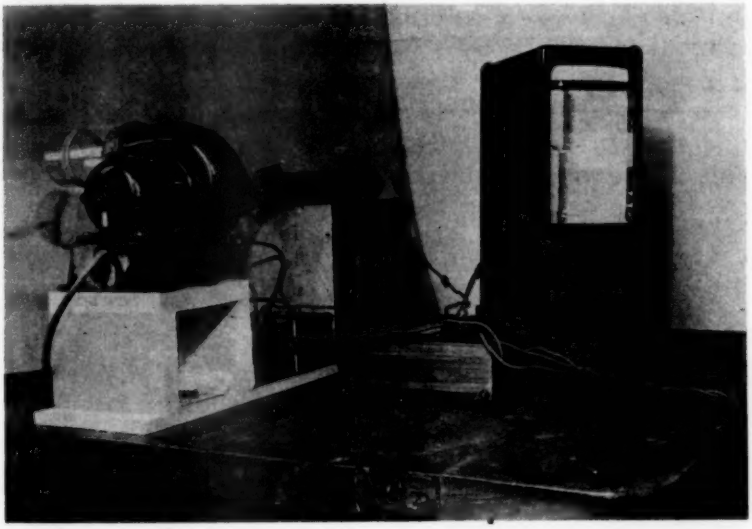
1.4×10^8. The rate of air flow was 5 L/sec. Accordingly, the number of ions/cc.

$$n = \frac{\Delta i}{25 \times 10^{-6}} \times \frac{1}{1.4 \times 10^8} \times \frac{3 \times 10^9}{4.77 \times 10^{-10}} \times \frac{1}{5000} = 3.6 \times 10^{11} \Delta i$$

or 3.6×10^5 ions per microampere change in plate current.

By modifying this circuit slightly, it has been possible to measure the normal atmospheric ion content and to record it automatically. A photograph of the apparatus is shown in Fig. 7.

FIG. 7.



In the case of the normal atmospheric ion content, the current to be measured is very small. This would involve the use of extremely high grid resistances which, although perfectly feasible, would not be desirable in an automatic device which must operate over long periods without attention or adjustment. Accordingly, instead of measuring the steady current, air is passed through the collector for a given interval and the accumulated charge is measured. Insulation troubles

are avoided by making the inner collector of two mil sheet nickel so that its weight can be supported entirely by the grid lead. Thus the only insulation to be reckoned with is that of the amplifier tube itself. This is of the order of 10^{15}. The grid lead passes through a 3/16 inch hole in the cover of the shielded amplifier box. Except for this opening, the box is air tight so that the glass surface can be kept in a clean dry condition by a small amount of drier. The electrostatic C of the collecting electrode plus the grid of the amplifier tube was determined experimentally and found to be

$$27 \times 10^{-12} F.$$

If air with an ion content of 50 ions/cc. is drawn through this collector for thirty seconds at the rate of 5 liters a second, and all of the ions entering are caught, the total charge accumulated will be

$$\frac{30 \times 5000 \times 50 \times 4.77 \times 10^{-10}}{3 \times 10^{9}} = 1.2 \times 10^{-12} \text{ coulombs.}$$

This charge will raise the potential of the collector and grid

$$\frac{Q}{c} = 0.04 \text{ volt.}$$

Thus a tube, such as the FP-54, having a mutual conductance of 25×10^{-6} amps./v., gives a change in plate current of 10^{-6} amps. for air having an ion content of 50 ions/cc. The amplifier circuit is shown in Fig. 8.

A commutator driven by a telechron motor supplies the means for grounding the grid and then allowing it to float and assume the potential determined by the charge collected. Two little projections on the commutator make contact with a little brush on the grid lead for two seconds every half minute. For the remainder of the time, the grid is free. The pressure of the brush is very slight and the motion of the commutator is slow so there is no tendency to give the grid a charge due to friction. During the first half minute of the cycle the grid floats to a potential determined by the leakage of the tube, it is then grounded for two seconds and then floats again for half a minute. During this part of the cycle, however, a blower, which is controlled by another

FIG. 8.

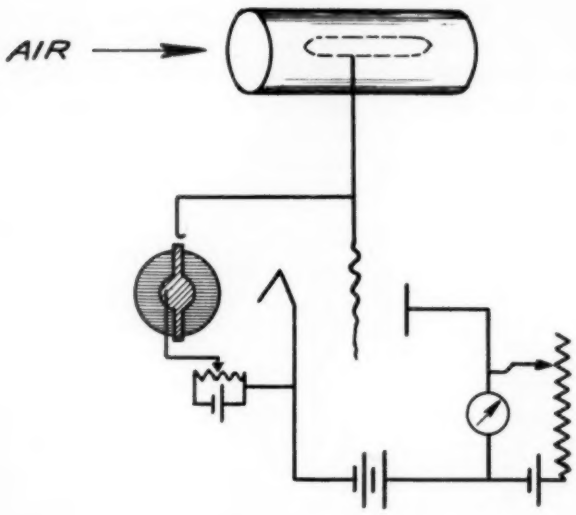
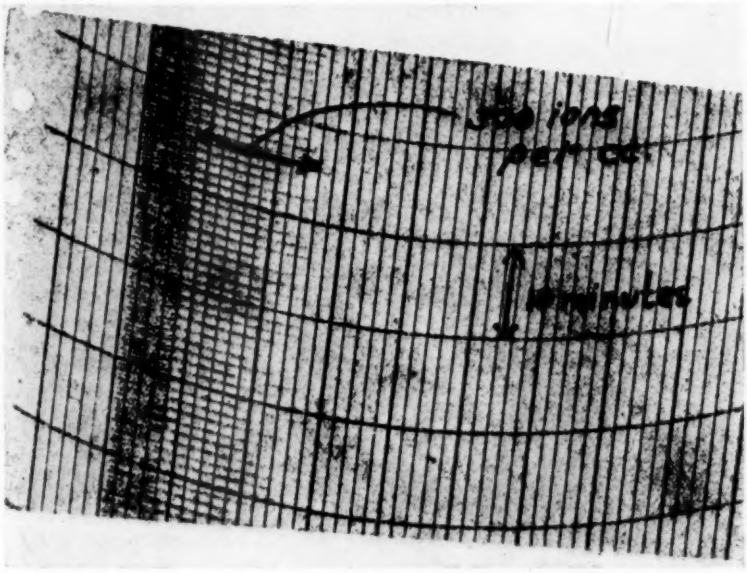


FIG. 9.



commutator on the same shaft, is set in operation and draws air through the tube and the grid assumes a potential determined by the number of ions collected from the volume of air drawn through. Thus, during each minute one reading of ion content is made and one of the leakage which is in effect the zero of the instrument. Thus any drift due to changes in the amplifier or in the battery voltages can be neglected since the zero is determined for each reading.

Since it is the change in amplifier current which is measured, it is desirable to balance out the steady current which is done by means of the auxiliary circuit consisting of the battery *D* and the resistance *R*. This circuit is stabilized by shunting *D* with a resistance equal to that of the vacuum tube filament. The indicating instrument used is a microammeter having a full scale deflection of 20 microamperes. For the purpose of making records, a photoelectric recorder has proved to be very convenient. A record of the ion content in a large room in the Research Laboratory over a 40 minute period is shown in Fig. 9.

The means are thus available for measuring and controlling the ion content of the atmosphere in rooms. It remains to be determined what bearing the ion content has on health and whether or not it is desirable to control it.

FINE STRUCTURE IN X-RAY ABSORPTION SPECTRA.*

BY

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The new experimental facts concerning the fine structure which occurs in X-ray absorption spectra, and the recent theoretical interpretations of it have been in such a direction as to link it with other modern developments in physical theory. It is, apparently, another example of a phenomenon which is only understandable in terms of wave-mechanics.

The first work in X-ray absorption spectra indicated that it was a very simple phenomenon. Discontinuities in the absorption coefficient were observed at wave-lengths corresponding to the inner Bohr energy levels of the atom. The K absorption edge, for example, is interpreted as being due to the sudden increase in the absorption coefficient for those quanta whose energy is just sufficient to eject an electron from the K shell out of the atom. Further experimentation, however, has shown that a fine structure exists at some of these principal absorption edges, and one is therefore led to consider what additional processes may be taking place, or what may be the nature of the end state of the ejected electron.

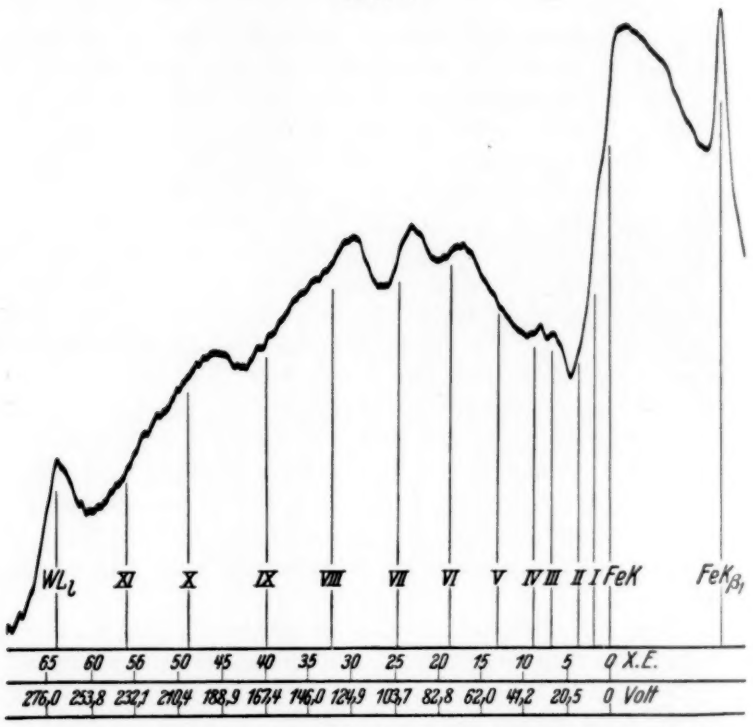
In Fig. 1 is illustrated what is meant by fine structure in X-ray absorption spectra.[1] This plate shows a microphotometer trace of the absorption spectra of iron in the region of its K edge which falls at 1739 X.U. The direction of shorter wave-lengths in this figure is to the left. It can be seen that at the point K the absorption suddenly increases

* Presented as an invited paper at the Symposium on X-rays of the American Physical Society at Yale University, June, 1932.

[1] The terms "fine structure," "secondary absorption," "multiple absorption," etc. have been variously used in the literature to designate different regions of the structure, but because of the qualitative nature of the distinction between them and the uncertainties of interpretation these terms are not separately defined in this paper.

and that in a region of about 60 X.U. or 250 volts on the shorter wave-length side of this main edge there are maxima and minima in the absorption coefficient of somewhat lesser magnitude. It should be explained that the general trend of the curve, showing the maximum in the middle and decreasing to both sides is not significant as this simply represents the

FIG. 1.



K X-ray absorption spectra of iron. (Direction of decreasing wave-lengths is to the left.)

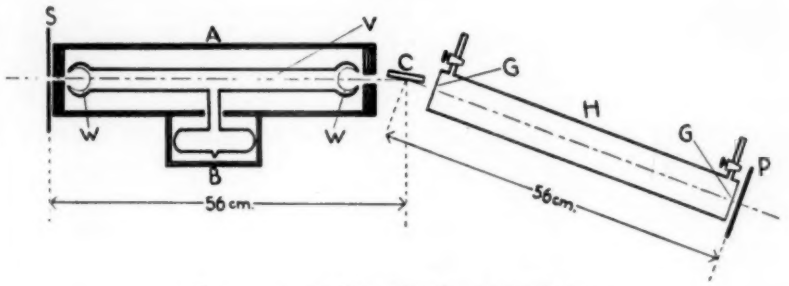
intensity distribution in the incident radiation before absorption.

The first explanation of the origin of the fine structure close to the main edge was by Kossel [2] who suggested that it represented the transitions of the electrons to various of the

[2] W. Kossel, *Zeit. f. Phys.*, **2**, 470, 1920.
See also Manne Siegbahn, Spektroskopie der Röntgenstrahlen, 1931, page 380.

outer unoccupied, or virtual, orbits of the atom. Obviously this idea could not account for those discontinuities which occur at energy distances of several hundred volts from the main edge. To explain the origin of this fine structure Lindsay, Coster and others have used the hypothesis of the simultaneous transitions of two or more electrons due to the absorption of a single quantum. A qualitative agreement between the location of the secondary discontinuities and the energies involved in simultaneous electron transitions has been shown for some substances.[3] However, for several reasons this procedure does not seem very satisfactory. In particular, it gives no understanding of the facts which are brought out by a study of the effects of physical and chemical state on the absorption spectra.[4] It appears also entirely untenable with the "temperature effect" of the absorption spectra.[5]

FIG. 2.



X-ray spectrograph for absorption spectra of vapors.

In Fig. 2 is shown the apparatus as used for the study of the absorption spectra of vapors. In order to study vapors, one must have a cell which will transmit the radiation, which will stand the requisite temperature to secure sufficient vapor density, and which will not react with the hot vapors. In the figure, S is the slit, C is the calcite crystal, and P is the photographic plate. The furnace B is for controlling the

[3] G. A. Lindsay and H. R. Voorhees, *Phil. Mag.*, **6**, 910, 1928. D. Coster and M. Wolf, *Nature*, **124**, 652, 1929. B. Kievit and G. A. Lindsay, *Phys. Rev.*, **36**, 648, 1930.

[4] J. D. Hanawalt, *Phys. Rev.*, **37**, 715, 1931.

[5] J. D. Hanawalt, *Zeit. f. Phys.*, **70**, 293, 1931.

vapor pressure, and the furnace A is for superheating the vapor. The cell V can be made of pyrex or of quartz. The concave windows W can be drawn to less than 5 μ in thickness and yet maintain a vacuum and stand temperatures to the melting points. H is a glass tube with windows of gold-beaters skin. The air is flushed out with hydrogen simply to reduce the air path of the radiation. The dispersion of this spectrograph in the region worked varies from 5.3 to 4.9 X.U. per mm., and the resolution from 7 volts to about 1 volt.

A comparison of the absorption spectra of an element in different chemical combinations both in the vapor state and in the solid state reveals the following facts:

1. The fine structures of a polyatomic vapor and of the same material in the solid state are usually similar, though the solid exhibits an additional structure not seen in the vapor spectrum. The examples of this are the As spectrum in As_2O_3 and in $AsCl_3$, and the Se spectrum in SeO_2. A comparison of the Br absorption in $NaBrO_3$ in solid and in solution shows that there is an additional structure in the solid not exhibited by the solution.[6]

2. The fine structure of a polyatomic vapor may differ from that of the solid. As_4 which is tetratomic in the vapor state is an example.

3. Fine structure of more than a few volts separation from the main edge is not observed for any monatomic vapor. This statement is based on observations on Hg, Zn, Xe and Kr, and one might also include in this list Ar which was studied by Coster and Van der Tuuk.[7] It is important to note that all of the fine structure which appears for monatomic vapors is of such energy that it may be explained as simply due to the transitions of electrons to the virtual orbits of the atom.

4. Fine structure is not observed in the spectra of the polyatomic vapors Se_8 and AsH_3.

5. The fine structure exhibited by Hg in $HgCl_2$ in solid

[6] This is contrary to the results of H. Th. Meyer, *Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern*, **7**, 101, 1929.

[7] D. Coster and J. H. Van der Tuuk, *Zeit. f. Phys.*, **37**, 367, 1926.

and in vapor forms has the same energy separation from the principal edges in both its L_{111} and its L_{11} spectra.[8]

6. In the series As, $AsCl_3$, As_2O_3, As_2O_5 and AsH_3 the principal edge has the same wave-length for the vapors while there are shifts of 5.5 ± 1.5 volts for the solids. Other characteristics of the fine structure might be listed[9] but enough has been mentioned to convince one that not only is the character of the fine structure determined by the nature of the surrounding atoms but also its actual existence seems conditioned by them, since while polyatomic vapors often display an extensive fine structure monatomic vapors never do. One concludes that fine structure represents a property of the atomic aggregate rather than of the atom.[10]

More facts concerning the nature of fine structure are afforded by a temperature study of the absorption of iron. This experiment was carried out at large dispersion using the same spectrograph as for the vapor studies with the arrangements as shown in Fig. 3. The iron foil, 5 μ thick, is heated in a vacuum cell by means of a conduction current and is held at the required temperature throughout the course of an exposure.

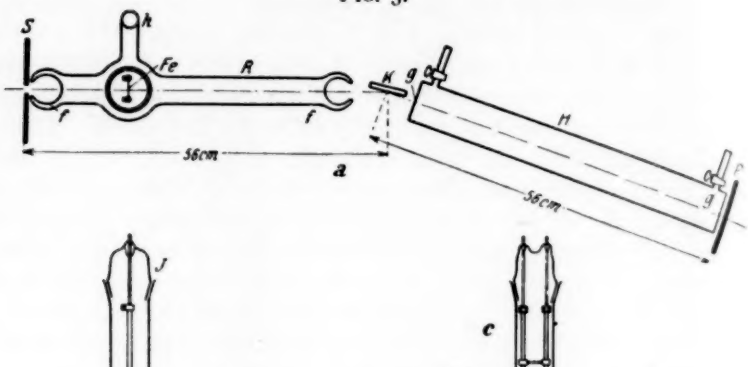
Figure 4 shows the absorption spectra obtained at different temperatures. The microphotometer traces *a* and *b* are of two plates when the iron was held at 20° C., while the traces *c* and *d* represent the absorption at 770° C. and 840° C. respectively. The first thing which one notices in this figure is that the fine structure has almost entirely vanished at the

[8] Practically all absorption fine structure recorded in the literature lies in the K spectra. However, the L fine structure reported is as follows: L_{111}, fine structure of compounds of the rare earths, Y. Nishina, *Phil. Mag.*, **49**, 521, 1925. L_{111}, fine structure of Pd_2H, J. D. Hanawalt, *Proc. Nat. Acad. Sci.*, **14**, 953, 1928. L_{111} and L_{11}, fine structure of compounds of Hg, J. D. Hanawalt, *Phys. Rev.*, **37**, 715, 1931. L_{111}, fine structure of Pt and Au, D. Coster and J. Veldkamp, *Zeit. f. Phys.*, **74**, 191, 1932.

[9] For a summary of the earlier work, and particularly for the discussion of the factors which determine the position of the principal absorption edge, see Manne Siegbahn, "The Spectroscopy of X-rays," and A. E. Lindh, Hand. d. Exp. Phys., Vol. XXIV, Part 2.

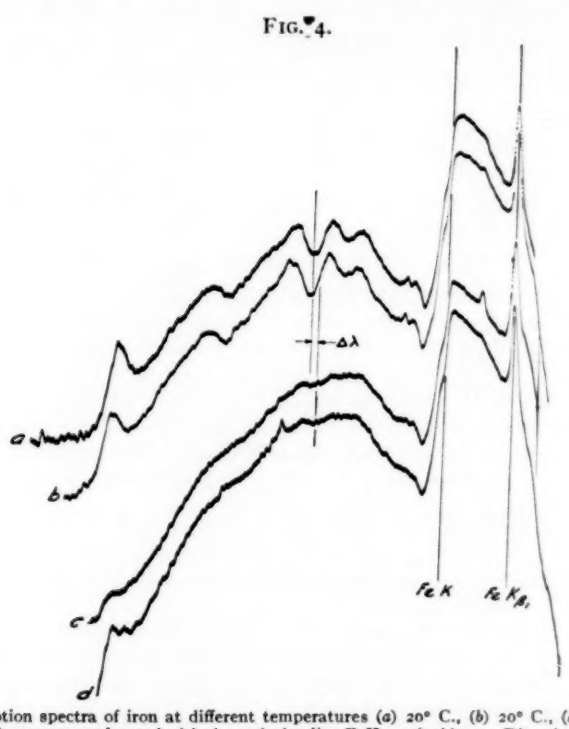
[10] It has been postulated by D. Coster and M. Wolf, *Nature*, **124**, 652, 1929, and by R. Swinne, *Phys. Zeit.*, **30**, 523, 1929, that fine structure will not be exhibited by atoms having completed electron shells. However, exceptions to this statement have since been shown.[4]

FIG. 3.



X-ray spectrograph for absorption spectra of solids at high temperatures.

FIG. 4.



Absorption spectra of iron at different temperatures (*a*) 20° C., (*b*) 20° C., (*c*) 770° C., (*d*) 840° C. The curves are located with the emission line $FeK\beta_1$ coincident. Direction of decreasing wave-length to the left.

higher temperatures except for the structure immediately at the principal edge. But perhaps still more interesting than this vanishing of the structure is the fact that there is also a shift of the positions of the maxima and minima of the fine structure in the direction of longer wave-lengths as the temperature is raised. Spectra obtained at 660° C. and 720° C. show that both of these effects are continuous as the temperature changes. Enough of the strongest absorption region remains at 800° C. to permit a measurement of the shift $\Delta\lambda$ which amounts to about 1.2 X.U. or 5 volts at a point which is about 115 volts from the principal edge, K. We shall return to a discussion of this shift after considering the theory.

Kronig has shown that the experimental facts concerning fine structure may be understood from the theory of the quantum mechanics of electrons in crystal lattices.[11] The basis for this theory lies in the idea introduced by Bloch [12] that for the explanation of the electrical properties of metals one can replace the influence of the crystal lattice on the weakest bound electrons by a periodic potential field having the same period as the lattice. The theory shows that not every value of velocity is possible to the motion of electrons traveling through a crystal lattice, but rather that there exists an energy spectrum consisting of alternating zones of permitted and forbidden energies.

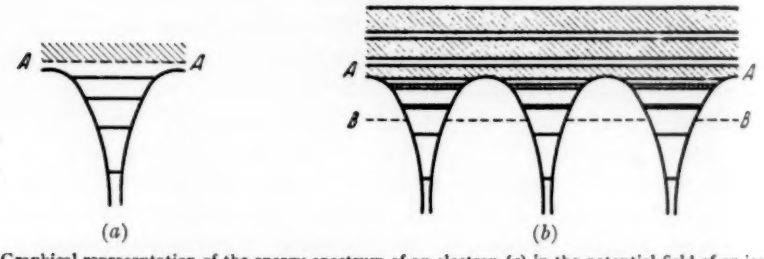
The difference in the situation for isolated atoms and for the crystal lattice is pictured in Fig. 5 taken from Kronig's paper.[11] In part (a) is represented the potential field of an isolated atom. The energy spectrum of an electron in such a field consists of discrete stationary states below the line AA; the lower of which represent the X-ray terms, and the higher the optical terms. Above the line AA the continuous region corresponds to free electrons or electrons which leave the atom with finite kinetic energy. The K absorption spectra of such an atom consists of a single edge corresponding to the transition of the electron from the K level to just outside the atom. The absorption coefficient on the short wave-length side of

[11] R. de L. Kronig, *Zeit. f. Phys.*, **70**, 317, 1931.
[12] F. Bloch, *Zeit. f. Phys.*, **52**, 555, 1928.

this edge has no discontinuities because the electron might in addition be given *any* value of kinetic energy.

In the crystal lattice the situation is quite different. Here the energy spectrum consists of permitted and forbidden zones of finite breadth. The lower permitted zones are very narrow and lie at about the same position as the X-ray terms of the isolated atoms, but at the higher energies the permitted zones become increasingly broader and the forbidden zones narrower. The important point for fine structure considerations is that this energy spectrum extends up into the region which is continuous for the case of the isolated atom. This means that free electrons traveling through the lattice cannot move with all values of velocity, but rather that certain values are forbidden corresponding to these forbidden zones.

FIG. 5.



Graphical representation of the energy spectrum of an electron (*a*) in the potential field of an isolated atom, (*b*) in a system composed of a periodic sequence of such potential fields. (Kronig.)

Accordingly in a crystal lattice the X-ray quantum can only eject an electron from the atom and thereby become absorbed if it gives the electron such a value of kinetic energy as to bring it into one of the permitted energy zones. Thus one will expect variations in the absorption coefficient, on the short wave-length side of the main edge, related to this sequence of permitted and forbidden energy zones. That this sequence of zones extends practically over only a finite region, and therefore that the extent of the fine structure is limited, is caused by the fact that at higher energies the forbidden zones have become so narrow that effectively only a continuous region is left. From observations of the extent of the fine structure region, one might conclude that electrons with kinetic energies greater than several hundred electron-volts

can travel through the lattice with practically any value of energy.

Kronig has shown that if a zero level of potential BB is so defined that the average potential in the crystal referred to this zero level vanishes, then the higher of the forbidden zones fall together with the energy values $W_n = \frac{n^2h^2}{8ma^2}$, where n is a whole number, a the distance between potential barriers, m the electron mass, and h Planck's constant. From this equation, as Kronig has pointed out, if the lattice constant a increases through thermal expansion the energy zones come closer to the zero level. Also, the impacts of the electron and lattice at higher temperatures become more frequent because of the greater distortion of the periodicity. This causes a smearing of the sharp boundaries between permitted and forbidden energy zones.

Thus we have an explanation of the two temperature effects as seen in the absorption of iron. The observed shift in the fine structure, as the following figures show, is in the right direction and is of the right order of magnitude. From X-ray measurements the lattice constant of iron at 20° C. is 2.86 Å, and at 800° C. is 2.90 Å, or an increase of .04 Å for this temperature change. The equation $\Delta W = e\Delta V = -\frac{n^2h^2}{4ma^3}\Delta a$ gives the change in energy ΔW for a change Δa in the lattice constant. If we put $\Delta a = .04$ Å and calculate ΔV in the region of $V = 115$ volts we find $(\Delta V) = -3.1$ volts which we see compares favorably with the experimental value of -5 ± 2 volts.

The reciprocal lattice constant squared form of the energy has since been verified in other ways. Lindsay[13] has investigated the K absorption spectra of potassium in the crystals KCl, KBr and KI. These crystals each have the same type of cubic lattice, but differ rather greatly in their absolute dimensions, the lattice constants being 3.139, 3.293, and 3.526 Å for KCl, KBr and KI respectively. Thus one should expect according to the theory: first, that the character of the fine structure exhibited by each of these crystals would be the

[13] G. A. Lindsay, *Zeit. f. Phys.*, **71**, 735, 1931.

same; and second, that the energy values of the corresponding discontinuities in the three absorption spectra would be proportional to the reciprocals of the squares of the lattice constants. How nearly this expectation is borne out is shown in Lindsay's table of data (Fig. 6). Table 1 gives the measurements on four points of the fine structure for each crystal. In Table 2 these distances have been multiplied by the square of the corresponding lattice constant. Complete agreement with the theory would then require that the three figures in each column be the same. The agreement is fairly satis-

FIG. 6.

Table 1. Distances in Volts

Crystal	$K-\alpha$	$K-A$	$K-\beta$	$K-B$
KCl . . .	9,7	14,8	20,7	26,6
KBr . . .	8,7	13,8	19,4	23,7
KJ	7,7	11,7	15,7	19,7

Table 2. Volts x d^2

Crystal	$K-\alpha$	$K-A$	$K-\beta$	$K-B$
KCl . . .	96	146	204	262
KBr . . .	94	149	210	256
KJ	96	145	195	245

Table.

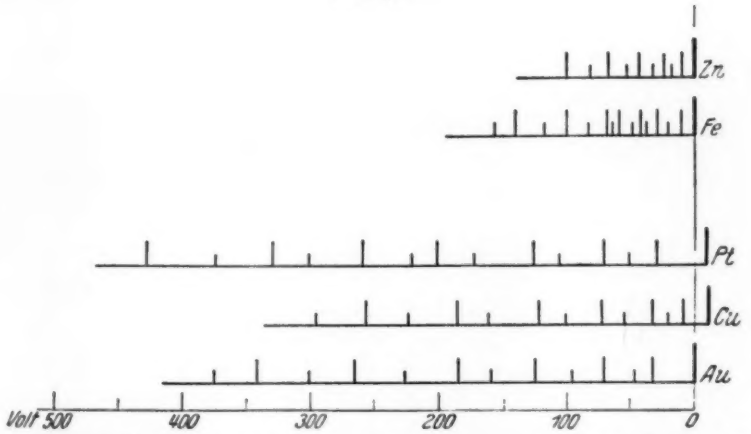
factory. The values of these figures depend upon the position chosen for the zero level, which in this case was taken as the principal edge.

Still further verification of the theory is afforded by the results of a series of very interesting experiments carried out by Coster and Veldkamp [14] on metals and alloys. They have obtained the fine structure of the absorption spectra of Pt and of Au in the regions of their L_{111} edges. In Fig. 7 is given their representation of these L spectra along with the K spectra of some other metals. The longer lines show the

[14] D. Coster and J. Veldkamp, *Zeit. f. Phys.*, **74**, 191, 1932; *Zeit. f. Phys.*, 70, 306, 1931.

positions of the minima of the absorption coefficients and the shorter lines of the maxima of the absorption coefficients, while the heavy line at the right represents the main edge. The separations of these maxima and minima from the main edge have all been reduced to correspond with the lattice constant of Au by multiplying each by the square of the ratio of the appropriate lattice constant to that of Au. Viewing the results for Pt, Au and Cu we see that the discontinuities in each of the three spectra fall approximately together if we allow a suitable arbitrary shift of the position of the main

Fig. 7.



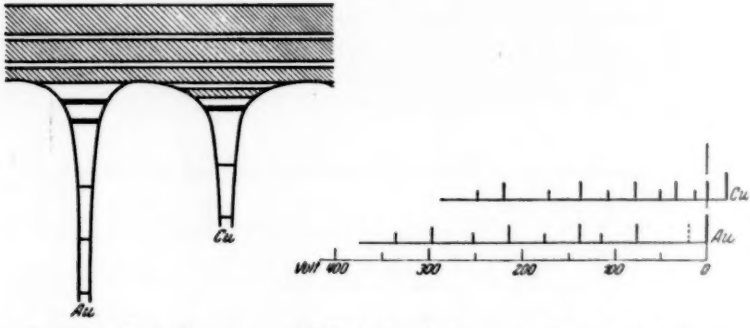
Distances of the minima of the absorption coefficients (long lines) and of the maxima of the absorption coefficients (short lines) from the principal edge (heavy line). The distances have all been reduced to correspond to the gold lattice by multiplication with $\left(\frac{a_x}{a_{Au}}\right)^2$. (Coster and Veldkamp.)

edges. Since each of these three metals crystallize in the F-C cubic system, the theory demands that their fine structures be identical when compared in this way. However, for a different type of crystal lattice one would expect a different type of fine structure, and this is seen to be the case for Fe which crystallizes B-C cubic and for Zn which crystallizes in the hexagonal system.

Still more striking results are obtained by Coster and Veldkamp from a study of a Au-Cu mixed crystal having 50 atomic per cent. of each element. They find that the maxma

and minima of the Au L_{111} spectra have shifted to higher energies, and the maxima and minima of the CuK spectra have shifted to lower energies by just such amounts that in the mixed crystal they have the same values. This is shown in their representation of the data given in Fig. 8. One concludes from these results that, as expected from the Kronig theory, the energy levels to which the K electron of Cu or the L electron of Au can be raised are the same when these elements are in this mixed crystal. This is represented by the schematic drawing of the forbidden and permitted energy zones in the Au-Cu mixed crystal. The lower levels of the atoms are about the same as in the isolated atoms,

FIG. 8.



Energy levels and absorption spectra for Au-Cu mixed crystal. (Coster and Veldkamp.)

but the higher levels merge into the permitted zones of the crystal lattice.

In addition to the *location* of the maxima and minima of the absorption coefficients, fine structure is characterized by their *magnitudes*. One might roughly express the intensity of the fine structure by giving the percentage by which the largest difference in the absorption coefficients at a maximum and at a succeeding minimum in the structure differ from the average absorption coefficient. The only quantitative measurements of this kind have been made by Coster and Veldkamp.[14] They found in the case of the Au-Cu mixed crystal that the intensity of the Au L_{111} fine structure was about the same as that of the Cu K fine structure, whereas

for these metals separately the Cu structure was about five times as intense as the Au structure.

Coster and Veldkamp's comparison of the K fine structures of Fe, Cu and Zn at room temperature shows intensities of 19 per cent., 13 per cent. and 7 per cent., respectively. We have seen that in the case of Fe as the temperature is raised the intensity becomes less and at 800° C. the structure has almost entirely disappeared. If we consider the respective melting points of Fe, Cu and Zn of 1530°, 1083° and 419° C., and therewith their respective distances from their melting points at room temperature, then perhaps the observed differences in intensity may be understood in terms of the temperature effect. This would also explain the otherwise rather baffling fact that the elements with low melting points such as Hg or Ga exhibit no structure.

However, the evidence on these points is not clear as yet. Coster and Veldkamp,[14] for instance, have recently found that for Zn the temperature must be raised to within about 20° of the melting point before any very noticeable weakening of the fine structure is observed, which fact stands in rather sharp contrast to the observations on Fe which showed that the structure had vanished at about 600° below the melting point.

Coster and Veldkamp have also shown that while the intensity in the L_{111} region of Pt is about twice that in the Au L_{111} spectra yet for both of these L spectra the intensities are much less than observed in the K spectra of elements of the same melting points. Whether the difference represents a characteristic of the K and L spectra or is some function of the atomic number has not been demonstrated as yet.

Kronig has very much further developed the theory of fine structure in a recent paper [15] in which he has investigated in how far it is possible to relate the individual minima of the fine structure, similarly as the lines of an X-ray powder diagram, to the various reflections of the electrons on the lattice planes. In this paper is calculated the perturbed energy of an electron traveling in a three-dimensional lattice, considering the energy of the free electron as a zero approximation. It is shown that there are discontinuities in the energy of the perturbed electron when the momentum

[15] R. de L. Kronig, *Zeit. f. Phys.*, **75**, 191, 1932.

components *abc* of the electron are related in a certain way to parameters $\alpha\beta\gamma$. This equation represents what may be called a discontinuity plane in the momentum space, and the parameters $\alpha\beta\gamma$ may also be thought of as defining planes in the *xyz* space or crystal lattice. This equation is namely the result derived by Morse [16] and by Brillouin [17] that there are discontinuities in the energy of the perturbed free electron when its direction of propagation with respect to the plane $\alpha\beta\gamma$ is such that the Bragg condition of reflection is satisfied. Kronig has shown, in spite of the fact that the values of these discontinuities or forbidden energy zones depend upon the direction of propagation of the electron, that after integration over all directions of propagation there are still finite variations in the absorption coefficient corresponding to each of these discontinuities. The energies of these discontinuities given in terms of α, β and γ are $W = \dfrac{(\alpha^2 + \beta^2 + \gamma^2)h^2}{8ma^2}$, which we see is the same equation as for the forbidden energy zones in the one-dimensional case but with n^2 replaced by $(\alpha^2 + \beta^2 + \gamma^2)$.

FIG. 9.

	Main Edge Volts.	B-β Volts.	C-γ Volts.	D-δ Volts.	E-ϵ Volts.
Theoretical.....	67	75	107	165	228
Experimental.....	11	59	106	168	246

Graphical representation of the theoretical calculations of the fine structure for copper. (Kronig.)

Figure 9 gives the result of Kronig's calculation for the Cu lattice. The abscissa S is $(\alpha^2 + \beta^2 + \gamma^2)$ and so represents the energy except for the factor $h^2/8ma^2$ which for Cu is 2.89. The values of $\alpha\beta\gamma$ used are determined by the sequence of planes which occur in the Cu lattice. At those values of S

[16] P. M. Morse, *Phys. Rev.*, **35**, 1310, 1930.
[17] L. Brillouin, *Journ. de Phys.*, **1**, 377, 1930.

for which there is a discontinuity in the energy, a rectangle is placed having the width two and a height proportional to the frequency with which the particular family of planes $\{\alpha\beta\gamma\}$ occur in the crystal. $S = 0$ gives the zero level which has been defined as lying at the position of the average potential in the lattice. The existence of a minimum energy $\overline{W}$ below which no discontinuities occur rests upon the fact that below this energy the energy states are filled so no transitions can take place. Kronig's theoretical calculation of $\overline{W}$ gives a value of 67 volts as compared to a value of 11 volts obtained by taking the difference between the experimentally determined average potential in the metal (from electron refraction), and the thermionic work function.

As can be seen in Fig. 9, the individual discontinuities lie closer together than is observed in the experimental spectrum. However, the discontinuities are more dense in some regions than in others and might be grouped together as shown in the figure. The table gives the comparison of the energy values of these regions with the observed experimental fine structure. A similar calculation of Kronig's for iron yields the same result, that is, that it is not possible to correlate the maxima and minima of the experimental absorption spectra to the individual discontinuity planes $(\alpha\beta\gamma)$. However, while a decisive agreement of theory and experiment is not reached in this way the principal predictions of the theory are consistent with the experimental results as they are now known. The latter are very incomplete and much in need of refinement and extension.

We have not discussed in the preceding the fine structure exhibited by polyatomic vapors. While it is true that the structure shown by vapors differs in details from that displayed by the same substance in the solid state, yet the outstanding observation is the high degree of similarity between them.[4] This fact probably means that the same explanation should be applicable to both of them. The outlines of a method of handling the case of polyatomic vapors has recently been given by Kronig.[18]

There is an effect, which has not been mentioned in this paper, which in particular cases produces the appearance of a

[18] R. de L. Kronig, *Zeit. f. Phys.*, **75**, 468, 1932.

limited fine structure. In chemical compounds in which the same element exists in two or more different energy states, e.g. having different valences, then the resulting superposition of the main edges having wave-length values different from each other will produce a simple structure.[19, 20]

To summarize briefly, we have considered the Kronig idea that following the ionization process the ejected electron must travel in the periodic potential field of the crystal lattice in the quantum mechanically prescribed way. This theory permits one to understand the principal experimental observations, namely: (*a*) The absence of fine structure for isolated atoms, and the dependence of fine structure upon the atomic aggregate, (*b*) the temperature effect of the vanishing of the structure, (*c*) the temperature effect of the wave-length shift of the structure, (*d*) the $\frac{1}{a^2}$ form of the energy, (*e*) the identity of the fine structures of different elements in the same crystal, and (*f*) the close relation of the character of the structure to the crystal structure of the substance.

[19] J. D. Hanawalt, *Proc. Nat. Acad. Sci.*, **14**, 953, 1928.
[20] Manne Siegbahn, "Spektroskopie der Röntgenstrahlen," 1931.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THE RECONVENING OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS.

The International Commission for Uniform Methods of Sugar Analysis deals with all matters of international importance relating to the scientific and technical aspects of the world's sugar industry, including standards, physical constants, and analytical methods. It is especially concerned with those factors which enter into the determination of value in the buying and selling of sugars. There have been seven previous sessions of the commission, the first being held in Hamburg in 1897, the last in New York in 1912. Owing to conditions which developed following the war it was found impossible, despite many urgent questions pressing for solution, for the commission to be reconvened.

As a result of numerous requests, including an urgent one made shortly before his death, by Dr. Alexander Herzfeld, president of the commission, the Bureau of Standards through Frederick Bates, chief of the bureau's polarimetric work, undertook the rehabilitation and reorganization of the commission. A comprehensive program was prepared covering 14 major subjects, and referees and associate referees from the world's leading authorities in each subject were appointed. After a year and a half of correspondence between these committees to eliminate minor international disagreements, the bureau made the announcement that the eighth session of the commission would be held in Amsterdam, The Netherlands, the week of September 5, 1932.

In order that the commission might function systematically a constitution and by-laws had become of fundamental importance, and especially was this the fact to determine the voting power of each of the nations in the commission. A suitable instrument was finally prepared at the bureau and Mr. Bates visited the principal European countries in advance

* Communicated by the Director.

of the session at Amsterdam and succeeded in eliminating practically all international objections. As a result of this procedure the constitution and by-laws were adopted immediately the session convened, and the commission for the first time in its history had a definite rule of procedure. In the 20 years that had passed since the seventh session, many important changes had taken place in the world's sugar industries. New scientific methods had sprung into use in the different countries and a great mass of new information had been evolved as a result of intensive research following the war. With the assembly of the delegates at Amsterdam it became evident that the elimination of differences and the adoption of international agreements on the principal subjects of the agenda were imperative.

The sessions, lasting four days, were conducted in English, French, and German, with a member of the bureau's staff presiding. To the surprise of everyone, in view of present economic conditions, approximately 50 delegates assembled at Amsterdam. They represented most of the principal sugar-producing sections of the world and included many of the principal organizations from the different countries as well as representatives from the Physikalisch-Technische-Reichsanstalt, the National Physical Laboratory, the Czechoslovakian Sugar Institute, the German Sugar Institute, the British Government's chemical laboratories, and industries using sugar products. Owing to the method of procedure which had been adopted in eliminating minor international disagreements prior to the session, it developed that the entire time of the commission at the sessions could be concentrated on major disagreements in the various subjects. Whenever it was impossible to arrive at definite conclusions during the time allotted on the program to a given subject, the discussion was closed and the referee and associate referees, together with other members vitally interested, were requested to hold night sessions and to continue until agreement was reached. The subject was again brought before the commission on the last day of the meeting. As a result, definite conclusions and recommendations were adopted in all the subjects on the agenda and provision made for such additional research as certain unsatisfactory methods indicated to be necessary.

In addition to the adoption of a constitution and by-laws, the commission adopted the Bureau of Standards numerical values for the standardization of the saccharimeter. The presence of the error in all instruments on which the world's sugar is bought and sold resulted in sugar testing more than one-tenth of 1 per cent. lower than it should. Despite the fact that practically all buying and selling of sugars continued on the old basis, the error was corrected by the Secretary of the Treasury in all instruments used in the United States Customs Laboratories. The increased revenue resulting from imported sugars as a result of the correction of this error has been very large. It is now a source of satisfaction that the International Commission for Uniform Methods of Sugar Analysis has recognized the correctness of the Bureau of Standards work and has adopted the bureau's physical constants covering the entire subject of the polariscopic testing of sugars.

One of the most attractive features of the meeting was an extensive exhibit of new equipment for scientific use in research on the sugars. This exhibit consisted principally of the latest types of optical instruments, most of which were set up for demonstration. It included exhibits from England, Holland, Germany, and Czechoslovakia.

Everything possible for the comfort and convenience of the delegates had been arranged by the Dutch authorities. Splendid excursions were provided and a farewell banquet was tendered the commission by the Algemeene Technische Vereeniging Suikerfabrikanten en Raffinadeurs of the Netherlands. The commission adjourned September 8th to meet in London in 1935 with the following officers: Frederick Bates, president; L. Eynon (London), secretary; and F. Tödt (Berlin), treasurer. The day following adjournment was given over to a trip to the Zuider Zee. This vast project for reclaiming the bottom of the ocean on a scale never before attempted by man is one of the world's most interesting and instructive engineering projects. The return trip to Amsterdam was not completed before nightfall, and the members of the commission carried away with them a profound respect for the enterprise and ability to work manifested by the people of the Netherlands.

SECOND INTERNATIONAL CONGRESS ON LIGHT.

The Second International Congress on Light, dealing with all questions of biological and biophysical researches in the fields of light and light therapy, was held in Copenhagen, Denmark, on August 15 to 18, 1932. Dr. W. W. Coblentz of the Bureau of Standards attended the congress as the United States member of the International Committee on Measurement and Standardization and as the representative of the council on physical therapy of the American Medical Association. For the latter organization he visited various heliotherapy stations in France, Switzerland, Germany, Denmark, and England, to learn their procedure, and, en route, he made ultra-violet measurements with a portable dosimeter which had been calibrated against the bureau's standard instruments.

Four principal subjects were considered by the congress: (1) How can the effect of light baths on tuberculosis be explained?; (2) The basis and organization of helioclimatic researches in relation to public hygiene; (3) The rôle of pigmentation in the biologic action of light, and the therapeutic effect of light baths; and (4) The choice of a unit and a method of measuring ultra-violet radiation used in medicine. Many other special papers were presented in the fields of physics, biology, therapy, and biochemistry.

Considering only the results of the deliberations of the committee on measurement and standardization, these may be summarized as follows.

It is recommended that ultra-violet radiation stimuli be evaluated upon a physical (radiometric) basis in absolute units. The ultra-violet radiation from the source is to be separated into three components by means of a non-selective radiometer (thermopile) and a series of three standard filters. The specifications for these filters are provisional, and may undergo slight changes with future developments. Dr. Coblentz is assigned the task of preparing and standardizing the filters, sets of which will be deposited at the following national research laboratories.

Bureau of Standards, Washington, D. C.
Comitade Nazionale della Richerche de Rome.
Institut d'Actinologie, Paris.

Institut Finsen, Copenhagen.
Institut für Strahlenforschung, Berlin.
National Physical Laboratory, Teddington.

If possible, these laboratories will deliver the filters to manufacturers, physicians, and meteorologists.

The committee recommends to physicians the use of simple methods of measurement (biological, photochemical, or photoelectrical) to control the constancy of each lamp used, and emphasizes that at the present time a comparison is only possible for the same lamp and not between different lamp types.

A definite decision as to the unit of measurement for the "ultra-violet used in medicine" could not be reached at the present congress. A program of coöperative research between the national laboratories is to be arranged, to serve as a basis for discussion at the next congress which will be held at Wiesbaden, Germany, in 1936.

The committee will publish a bibliography of actinometric papers of interest to biologists and physicians.

The members of the international committee are to inform the medical societies and scientific journals of their countries, concerning the above recommendations. While the recommendations are not without some ambiguities, they are a long step in the right direction.

While only filters are mentioned in the recommendations, for precise work it will be desirable to use a water cell in front of the thermopile to eliminate differences in the infra-red absorption by the filters.

As to the results of the conference, it was evident that in a field so new it is not yet possible to entirely subordinate personal preferences. It was, therefore, not possible to formulate a broad, general procedure which will be best for the future. Thus the question whether the specification of dosage should be on a physical or a correlated biological (erythemal) basis, while discussed at the first congress in 1929, is still so new that the physiologists and phototherapists could not reach an agreement.

In this country the evaluation of radiation stimuli in energy units (microwatts per cm.^{2}) was begun about 18 years

ago, and is now in common use. Recently these energy measurements have been correlated with the erythemogenic effectiveness of various types of ultra-violet lamps on a limited number of healthy persons having average skin pigmentation. This forms the basis of the specification for minimum intensity of ultra-violet adopted by the Council on Physical Therapy of the American Medical Association.

As already stated, the International Congress on Light will meet again in 1936. The present indications are that, in the meantime, there will be much greater international coöperation, and when the committee on measurement and standardization again meets, those present should have ample information and data available upon the questions now awaiting action.

SHEAR TESTS OF REINFORCED BRICK MASONRY BEAMS.

Beams of reinforced brick masonry were tested at the bureau to obtain data on their resistance to failure by diagonal tension. Tests were made also of the compressive strength of small masonry piers and of the bond strength of the mortar to the bricks and steel reinforcement. The investigation was carried out with the coöperation of the Common Brick Manufacturers' Association.

Eighteen beams were tested, each being 14 feet long and about one foot square in cross section. Nine of the beams were built with common brick from Chicago and the other nine with common brick from Philadelphia. In one type of beam the bricks were laid in common American bond, as in a 12½ inch wall; in another the bonding was similar to that in a lintel beam with a soldier course forming the lower portions of each face of the beam, over which were laid two stretcher courses. The third type was built on end with vertical reinforcement to resemble a portion of a 12½ inch retaining wall with all bricks laid as stretchers. A 1 : 3 Portland cement-sand mortar, with an addition of lime equal to 15 per cent. of the volume of the cement, was used for all beams. Each beam contained six 1/2-inch square bars as tensile reinforcement. Tests were made when the beams were one month old.

The positions of the neutral axis in the beams varied with the kind of brick, the arrangement of the bricks in the beam,

and the loads. The ratio between depth to neutral axis and depth of the tensile reinforcement increased with an increase in the number and total thickness of the mortar joints in the masonry. The position of the neutral axis corresponded to that calculated by means of the design formulas applying to beams of reinforced concrete, with an assumed modulus of elasticity of the masonry equal to 50 to 70 per cent. of that of the masonry piers.

The failures of all beams were accompanied by cracks near the ends of the beams, between a support and the nearer load. The cracks were evidence of failures by diagonal tension.

Maximum shearing stresses for the different types of beams ranged from 65 to 159 lbs./in.^{2} Resistance to diagonal tension increased with an increase in the proportion of the bricks laid with staggered joints. Shearing strengths of the beams were in the same order as shearing and tensile bond strengths of small masonry specimens.

With the relatively absorbent bricks used, the tensile and shearing strengths of the masonry were much greater when the bricks were wetted before laying than when laid dry.

Bond strengths as determined by pull-out tests of one-half inch square deformed bars embedded about 8 inches in brick masonry ranged from 870 to 950 lbs./in.^{2} Differences in the kind of bricks and curing conditions did not cause significant changes in bond strength.

A complete report of the investigation will be published in the December, 1932 issue of the *Bureau of Standards Journal of Research*.

COLLOID CONTENT OF ENGLISH CHINA CLAYS.

The relative colloid contents of several English china clays were determined by the water adsorption method, using hydrogen saturated samples of clays and colloids. The "colloid" fraction, obtained by means of a supercentrifuge, was made up of particles less than 0.8 micron in diameter. Samples of the original clays, and the colloid fraction obtained from each, were electrodialyzed to replace the adsorbed salts by hydrogen. Water adsorption of the dialyzed materials was determined over about 3 per cent. sulphuric acid at a tempera-

ture of 30° C. and under a pressure of less than 50 millimeters of mercury. The ratio of water adsorption per gram of clay to the water adsorption per gram of the extracted colloid was calculated to be the percentage of colloidal material in the clay. Following are the results obtained:

Clay.	Colloidal content. Per cent.
A	29
B	36
C	32
D	28
E	34
F	30
G	29
H	30
J	35
K	41
L	32
M	31
O	21

THE SYSTEM: $CaO.B_2O_3$.

The binary system: lime-boric oxide has been investigated, and the optical properties and melting points of the four calcium borates occurring in this system have been determined. This work was done as a preliminary to a study of part of the ternary system: lime-boric acid-silica, which was briefly outlined in Technical News Bulletin No. 157 (May, 1930), under the title "Effect of Boric Acid on the Clinkering of Portland Cement." The purpose of this work is to determine the effect of the addition of small amounts of boric oxide to the calcium silicates found in Portland cement. It is hoped that the results may prove of interest also in connection with the production of glazes and other ceramic materials.

Mixtures of lime and boric oxide, containing more than 23 per cent. lime, fuse to a clear liquid, while mixtures containing less than this amount form two layers which are immiscible even above 1500° C. One of the layers consists almost entirely of boric oxide, while the other contains 23 per cent. lime. Mixtures in this region do not crystallize readily, the boric oxide phase remaining permanently in the form of a glass.

The phase equilibrium diagram for the system was worked

out by means of heating curves. The melting points of the four compounds are as follows: calcium diborate, $Ca.2B_2O_3$, 982° C.; monocalcium borate, $CaO.B_2O_3$, 1151° C.; dicalcium borate, $2CaO.B_2O_3$, 1295° C.; tricalcium borate, $3CaO.B_2O_3$, 1475° C.; all temperatures being subject to an error of ± 5°.

EXPERIMENTAL TESTS OF MIMEOGRAPH PAPER.

Some tests made in the paper section of the bureau on the properties of wood fiber mimeograph paper may be of interest to other users of such paper. Some difficulty has been experienced at the bureau in obtaining mimeograph paper possessing both good printing and good writing quality. The printing at times offset badly despite extreme care in the printing operation, and when both sides of the paper were used lack of opacity sometimes caused the printing to have a very bad appearance. When both troubles occurred together, the printing was not very legible. The papers were sometimes so poorly sized that writing ink ran through them.

By laboratory tests of papers that had given both satisfactory and unsatisfactory printing results, definite measurable limits were established for the properties that appeared to be important. The better papers were bulky, had a rough finish, a medium amount of clay filler, a medium degree of water resistance, which is a measure of resistance to writing ink, and a high degree of opacity.

With figures for the required properties established, experimental tests were made in the bureau's paper mill to determine the papermaking procedure which would produce the desired type. The best results were secured with soda and sulphite wood fibers mixed in equal proportions; a moderate degree of rosin sizing; and the use of light pressures on the machine presses, without any final calendering, to obtain the desired bulkiness and rough finish. The characteristics of paper produced in this manner and having the desired printing and writing properties are shown by the following test data: Weight (25 × 40, 500)—57 pounds; thickness—0.005 inch; bursting strength—12 pounds per square inch; ash—8 per cent.; water resistance (dry-indicator method)—11 seconds; opacity—96 per cent.

NICKEL CHROMIUM ALLOYS FOR WEIGHTS.

In 1930 this bureau prepared sample weights from two lots of metal of an alloy of 80 per cent. nickel and 20 per cent. chromium, and from a metal denominated "nichrome," this alloy being about 60 per cent. nickel, 15 per cent. chromium, and 25 per cent. iron. To these were added later other samples made by a balance maker from an alloy said to be 80 per cent. nickel and 20 per cent. chromium. These sample weights were chiefly of 10 grams and 50 grams. Some were one-piece weights and most of the work was done on these; others were of the ordinary screw-knob type with a few small pieces of aluminum, copper, gold, etc., under the knob.

During the next two years some of these samples were kept under good atmospheric conditions, and handled only enough to make the necessary calibrations. The other samples were boiled in distilled water, were immersed in water twice for making hydrostatic weighings, were baked at 100° C., and were twice exposed to hydrochloric acid fumes in a closed space with a 20 per cent. solution of hydrochloric acid. After the acid exposures these samples were air dried and were wiped carefully and rather vigorously with dry cheesecloth.

The one-piece weights kept under good conditions seem to indicate a constancy sufficient for most high precision standards, as weights of 50 g. and 100 g. were constant within about one in 10^7, while weights from 20 g. to 2 g. showed no changes greater than 10 in 10^7.

In the weights subjected to boiling and to hydrostatic weighings the maximum change shown by those samples that had been thoroughly washed in benzol and in alcohol was 5 parts in 10^7. Others showed changes up to 60 in 10^7, but this is no greater than those that occur occasionally in high precision gold plated standards submitted for regular test.

The exposure to hydrochloric acid fumes was severe treatment, but not much if any more severe than sometimes occurs in chemical laboratories. This is indicated by the fact that some other samples, exposed at the same time, suffered changes comparable with the changes that had occurred when those samples were exposed in a chemical laboratory where acid fumes were strong. In the present exposures all four of the 50 g. samples lost from 0.5 mg. to 1.4 mg. after all deposit and

loose corrosion products had been wiped off with dry cheesecloth. The 10 g. samples lost 0.1 or 0.2 mg. The maximum loss on the screw-knob samples was 0.7 mg. In many cases weights gained amounts similar to these before they were wiped, even when there was no evident deposit of liquid on the surface. These changes amount to 2 or 3 in 10^5.

Although standard weights should not be exposed to acid fumes of appreciable concentration, it is also true that such weights should be made, if possible, of materials not seriously affected by such exposure. Moreover, hydrochloric acid fumes are very likely to occur in many laboratories. Therefore these large effects of acid exposure constitute a serious objection to the use of these nickel chromium alloys for precise standards. Nickel chromium weights seem likely to be seriously affected by hydrochloric acid fumes, no matter how well they are made. Therefore, in general specifications for the highest classes of standards, it seems reasonable to exclude such nickel chromium alloys.

It has been decided, therefore, that weights made of these nickel-chromium alloys should be considered as not conforming to the general specifications for high precision laboratory standards (Bureau of Standards Class M).

For less precise work, for which the usual high grade analytical weights are suitable, these alloys seem to meet the general requirements. Weights made of the alloys investigated may therefore be tested by the bureau under "Class S."

For the higher grades of commercial standards—Bureau of Standards Classes A, B, and C—a somewhat smilar distinction must be made, though on slightly different grounds. For Class A standards, which are used as primary standards for the States or for makers of commercial standards, the danger of corrosion is much less than for laboratory standards, but there are generally less chances for checking the constancy of the standards.

It seems best therefore (at least for the present) to exclude these nickel-chromium alloys from the materials allowed for weights of Class A, while for Classes B and C, which include what may be termed office and field test weights, this material is considered entirely satisfactory.

STANDARD TIME THROUGHOUT THE WORLD.

A publication of considerable general interest, which has just been released by the bureau, is Circular No. 399, "Standard Time Throughout the World." The new circular supersedes Circular No. 280 of the same title, and contains as complete information as is available on the present status of the use of International Standard Time. The paper includes a brief historical sketch of the development of the standard time system, a list of official stations in the United States which send out radio time signals, a list showing the legal time in practically every nation of the world, and maps ilustrating the International Time Zones.

Copies of this circular are obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C., at 5 cents each.

NOTES FROM THE BARTOL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE.

ELECTRONS AS COSMIC RAYS.*

Professor A. H. Compton's fundamentally interesting experiments on the variation of cosmic-ray intensity with latitude raises once more, as he suggests, the possibility of cosmic rays being electrons. In addition to the bearing of such a hypothesis upon variations with altitude and with latitude, certain other matters suggest themselves as interesting for consideration.

In 1924, in connection with a theory of the absence of ionization [1] by electrons of sufficiently high energy, the writer pointed out that an electron with velocity only 40 meters per second less than the velocity of light, i.e., with energy corresponding to 10^9 volts, could not approach the earth's surface at the equator nearer than a point at a distance of 8 earth's radii from the earth's center when projected from infinity towards the earth's surface in the magnetic equatorial plane. For the most favorable direction of projection in that plane at infinity, an electron would have to possess 10^{10} volts velocity in order to reach the surface. A. Bramley and the writer [2] having given evidence from the wave mechanics supporting the conclusion that electrons of energy comparable with this amount may be incapable of ionizing, as formerly surmised by the writer [1] for energies of the order 10^9 volts on the basis of the classical electrodynamics. Such a conclusion would render more reasonable an explanation of

* Reprinted from *Physical Review*, pp. 540–542, Vol. 41, No. 4, August 15, 1932.

[1] W. F. G. Swann, *Phil. Mag.* [6], **47**, 306–319 (1924). Very exhaustive treatments of the orbits of electrons in the earth's magnetic field have been given by C. Stormer on the theoretical side and by K. Birkeland on the experimental side, in papers extending as far back as 1904. These have to do chiefly with the positions of the auroral zones.

[2] W. F. G. Swann and A. Bramley, *Phys. Rev.*, **41**, 393 (1932). Read before the New Haven Meeting of the Am. Phys. Soc. on June 23, 1932.

the maintenance of the earth's charge by the influx of such electrons, since it would relieve us of the difficulty following from the large ionization which the 1500 electrons per square centimeter per second, necessary to account for the earth's charge, would otherwise cause. Another point of interest involves the idea that for such electrons, considered as primary cosmic radiation, the action of ionization would have to occur through the intervention of secondaries shot out only occasionally by the primaries. The operation of the primaries would thus become more closely comparable with that characteristic of photons.

The actual experimental observation of secondary electrons of energies comparable with 10^9 volts, by Professor Millikan and his collaborators, raises many interesting questions. Such electrons would describe, in the earth's magnetic field, circles or helices of radius 10^7 cm.; and their energy, on the basis of 16 volts per ion and 50 ions per centimeter of path at atmospheric pressure, would enable them to travel distances comparable with the whole thickness of the homogeneous atmosphere, and indeed distances forming at least appreciable fractions of the whole circumference of the circular orbits into which they are bent. The conclusions following from the foregoing considerations may best be illustrated in limited space by reference to Fig. 1, where in

FIG. 1.

each case the circle represents the complete orbit of the electron if there were no absorption in earth or air (for simplicity, we consider orbits in the magnetic equatorial plane). The dotted line represents the earth's surface, and the point *O*, the point of emission of a secondary in the atmosphere. Even for the case of symmetrical emission of secondaries by primaries in all directions in the lower hemisphere, there will not be symmetrical emission of secondaries with respect to a plane passing through the magnetic poles.

Thus, consider a case where the electron path (shown by the thick line) is one-eighth of the circumference. Corresponding to an electron striking the earth at 45° from east to west as in Fig. 1*A*, there will be an electron striking at 45° from west to east as in *B*. But corresponding to an electron striking tangentially from east to west as at *C*, there will be no electron striking tangentially from west to east. Such an electron would have to have come from below the surface of the earth as at *D*, and to have been emitted partially upwards. A lack of symmetry in favor of vertical emission of secondaries would enhance still further the considerations here cited.

The orbits of high energy electrons are determined entirely by their relativistic mass, and are otherwise independent of the velocity since that velocity is practically equal to that of light. Since the mass is proportional to the energy for electrons and protons of very high energy, the orbits will be the same for protons as for electrons of the same energy, if that energy is high enough, except that they will be described in the opposite sense.

It is of interest to observe that in the case of observations on a high mountain, radiations coming from electrons which have passed their lowest point should be directed slightly upwards. It is also of interest to note the shielding effect to be expected from a mountain *M* for such conditions as are represented in Fig. 1*E*.

W. F. G. SWANN.

BARTOL RESEARCH FOUNDATION OF
THE FRANKLIN INSTITUTE,
August 1, 1932.

ON THE RADIATION ORIGINATING FROM A BEAM OF ELECTRONS IN MERCURY VAPOR AND THE MEAN LIFE OF THE 2^3S_1 STATE.

BY

LOUIS R. MAXWELL, Ph.D.*

Previously the writer [1] has obtained photographs of the mercury spectrum produced by a beam of electrons in mercury

* Communication published in the *Physical Review*, **42**, 148 (1932), and represents work done as a fellow of the Bartol Research Foundation.

[1] Maxwell, L. R., *Phys. Rev.*, **32**, 715 (1928).

vapor. The optical arrangement consisted of projecting the image of the electron beam on to the slit of the spectrograph perpendicular to the length of the slit. It was found that some of the lines extended beyond the image of the electron beam, this being particularly true for the resonance line 2537 A. This result has recently been confirmed by Lees and Skinner.[2] The extension of the lines beyond the image of the electron beam is caused by the radiation of atoms lying outside of the boundaries of the beam. In Table I are included the

TABLE I.

Lines of the Mercury Arc Spectrum.

Lines extending beyond image of the electron beam.		Lines conforming to the width of image of electron beam.	
1^1S_0–2^3P_1	2537	2^1P_1–4^1D_2	4347
2^3P_0–2^3S_1	4047	2^1P_1–5^1D_2	3906
2^3P_0–3^3S_1	2752	2^1P_1–6^1D_2	3704
2^3P_0–3^3D_1	2967	2^1P_1–7^1D_2	3592
		2^1P_1–5^1S_0	3801
2^3P_1–2^3S_1	4358	2^3P_2–2^3S_1	5461
2^3P_1–3^3S_1	2893		
2^3P_1–4^3S_1	2576		
2^3P_1–2^1S_0	4077		
2^3P_1–3^3D_2, 3^3D_1	3125, 3131		
2^3P_1–4^3D_2, 4^3D_1	2653		
2^3P_1–5^3D_2, 5^3D_1	2482		
2^3P_2–3^3D_3	3650		
2^3P_2–3^3D_2	3654		

most prominent lines obtained which are classified into two groups; extended lines and normal lines. Figure 1 illustrates a typical spectrogram obtained. In this particular case the electrons were accelerated to a velocity of 200 volts. A transverse electric field was applied for the purpose of drawing out the spark line 4797 A as shown in Fig. 1. The shape of the lines was not particularly dependent upon the speed of the electrons. In general the lines having the levels 2^3P_0, 2^3P_1, 2^3P_2, as the final state are lengthened, whereas the lines terminating in the 2^1P_1 state do not show spreading beyond the image of the electron beam. An exception to this rule, however, occurs for the line 2^3P_2–2^3S_1 (5461 A) which does

[2] Lees, J. H., and Skinner, H. W. B., *Proc. Roy. Soc.*, **137a**, 186 (1932).

not show any appreciable elongation. The lines of the series 2^1P–n^1S_0 4916 A–4108 A, showed slight extension beyond the image of the electron beam, but the line 3801 A, 2^1P_1–5^1S_0 showed practically no spreading.

The lengthening of the resonance line (2537 A) is ob-

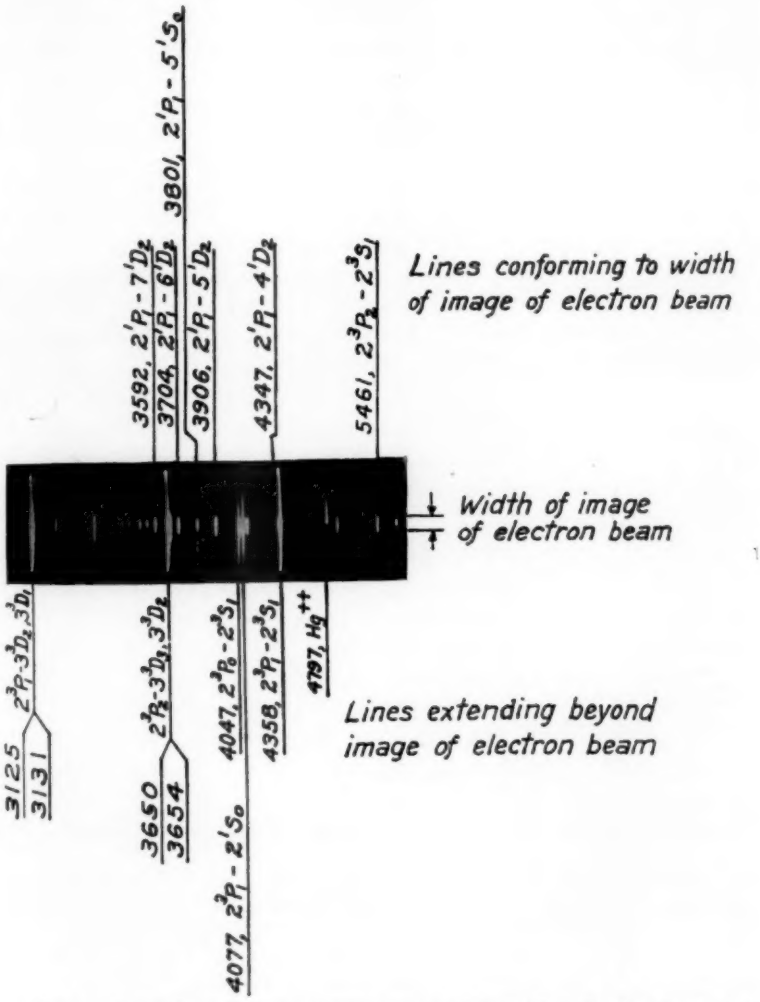


FIG. 1. A portion of the mercury spectrum illustrating the lengthening of lines beyond the image of electron beam.

viously caused by absorption since it is very easily absorbed at the pressures of about .001 mm. of Hg used in this case. It has been proposed [3] that the lengthening of the other lines was caused by absorption of atoms in the 2^3P_0, 2^3P_1 and 2^3P_2 state located in the vicinity of the electron beam.

Similar lengthening or spreading of spectrum lines has been found for helium [4] and for the case of the lines 2^3P–n^3D. Lees and Skinner suggested that it was caused by collisions of the type

$$\text{He}\,(n^1P) + \text{He}(1^1S) = \text{He}\,(1^1S) + \text{He}(n^3D)$$

occurring outside the electron beam where the energy differences between the n^1P and n^3D states are of the order of the thermal energy. For mercury, similar atomic collisions resulting in a change from n^1P_1 to $n^3D_{1,\,2,\,3}$ states may be possible. Transitions of this kind to populate the 2^3S_1 state from any of the n^1P_1 levels will be very unlikely on account of the large energy differences involved.

Randall and Webb [5] have measured the mean life of the 2^3S_1 state of mercury by using the lines 2^3P_2–2^3S_1 (5461 A), 2^3P_1–2^3S_1 (4358 A) and 2^3P_0–2^3S_1 (4047 A) and found that the lines 4358 A and 4047 A gave the mean life of 5.75×10^{-8} sec. while the line 5461 A gave an entirely different value of 2.37×10^{-7} sec. In this connection it is very interesting to notice from Table I that the line 5461 A which gave the greater mean life shows no lengthening while on the other hand the other two lines 4358 A and 4047 A have prominent spreading. This shows that outside of the electron beam there are atoms in the 2^3S_1 state which will give rise to transitions to the 2^3P_0 and 2^3P_1 levels but with practically the exclusion of transitions to the 2^3P_2 state. This undoubtedly means that the fine structure of the 2^3S_1 level plays an important part in the radiation phenomena, in support of the

[3] Maxwell, L. R., *Phys. Rev.*, **31**, 711 (1928); see also for instance, for absorption of excited states: Turner, L. A. and Compton, K. T., *Phys. Rev.*, **25**, 606 (1925); Wood, R. W., *Phil. Mag.*, **50**, 774 (1925); ibid., **4**, 466 (1927).

[4] Lees, J. H., *Proc. Roy. Soc.*, **137a**, 173 (1932); Lees and Skinner, loc. cit.; Maxwell, L. R. Early issue of JOUR. FRANK. INST.

[5] Randall, R. H. and Webb, H. W., *Phys. Rev.*, **35**, 665, 1161 (1930). See also Richter, E. F., *Ann. d. Phys.*, **7**, 293, 1930.

conclusion arrived at by Randall and Webb to account for the discrepancies found for the mean life of this state.[6]

There exists the possibility that the photograph plate characteristics may vary for the triplet lines in such a manner as to weaken the spread of the line 5461 A in comparison with the lines 4047 A and 4358 A, since the green line is nearer to the less sensitive portion of the plate. Exact intensity measurements were not obtained, however the difference in shape of the line 5461 A in comparison with the other lines of this triplet appears too great to be accounted for by errors of this kind.

This work was done in the laboratory of the Bartol Research Foundation.

THE VARIATION OF THE COSMIC-RAY INTENSITY WITH AZIMUTH.*

BY

THOMAS H. JOHNSON AND J. C. STREET,

Bartol Research Fellows.

We have measured the intensity of the cosmic rays at an angle of 30° with the vertical in the magnetic N., S., E., and W. azimuths using three G.M. counters as a telescope. The point of observation was the roof of the Bartol Research Laboratory in Swarthmore, Pennsylvania, latitude 40° N. The apparatus was protected from the weather by a covering of $\frac{1}{2}$ mm. thick sheet iron but was not otherwise influenced by absorbing material. The three counter tubes were arranged with their axes horizontal and perpendicular to the direction of observation. They were 12 cm. long, 4 cm. in diameter and were spaced at 10 cm. between adjacent centers. The circuits were arranged for recording triple coincidences and a previous observation had shown that the number of accidental coincidences was less than 0.1 per cent. of the real ones at this separation. Our results up to the present time are given in Table I with the statistical probable errors indi-

[6] For further discussions see Morozoroski, S., *Zs. f. Phys.*, **68**, 278, 1931; Frisch, R. and Pringsheim, P., *Zs. f. Phys.*, **67**, 169, 1931.

* Communication published in the *Physical Review*, **41**, 690 (1932).

cated. The barometric pressure at the middle of each run is also included.

TABLE I.

Direction.	Date.	Duration of Run, Minutes.	Barometer.	Number of Coincidences.	Coincidences per Minute.
E.	7–21	1040	759	939	0.90±0.02
W.	7–22	1380	756	1253	0.90±0.02‡‡
N.	7–23	1495	754	1445	0.97±0.02
S.	7–24	1370	760	1373	1.00±0.02
E.	7–25	1447	762	1207	0.83±0.02
W.	7–26	1418	760	1175	0.83±0.02
N.	7–27	1432	760	1244	0.87±0.02

The results show that the intensity is about the same in the E. and W. azimuths but the cosmic rays are from 5 to 10 per cent. more intense in the magnetic meridian than perpendicular to it. There is possibly a greater intensity towards the S than towards the N. Unfortunately the data show a variation of the counting rate with time which is probably instrumental but we believe the variation with azimuth cannot be accounted for in this way. These measurements are preliminary to a more complete investigation which is now in progress.

We wish to acknowledge the coöperation of Dr. E. C. Stevenson.

AN INTERPRETATION OF COSMIC-RAY PHENOMENA.*

BY

THOMAS H. JOHNSON.

Schindler's data on the transition effects of the cosmic rays have been interpreted on the assumption that the equilibrium between the primary radiation and its secondary corpuscular rays is different in different media. The ionization behind any thickness of absorbing materials, assumed to be proportional to the flux of secondaries, is calculated in terms of the absorption coefficients, $\nu(m)$, of the primary radiation and the production and absorption coefficients, $\beta(m)$ and $\mu(m, m)$, respectively, of the secondary rays, these coefficients being characteristics of the media. A comparison with the data

* Abstract of a paper published in the *Physical Review*, 41, 545 (1932).

permits a determination of each of the absorption coefficients as well as the product of each of the production coefficients by the number of primary rays. The results are as follows, expressed in cm.$^{-1}$ lead equivalent: ν(Pb) = 0.0064; ν(Fe) = 0.009; μ(Pb, air), the absorption coefficient in lead for secondaries produced in air = 0.50; μ(Pb, Pb) = 098; μ(Fe, air) = 0.30; μ(Fe, Fe) = 0.45; μ(Pb, Fe) = 0.72; μ(Fe, Pb) = 0.48; β(Pb)/β(Fe) = 2.0. This determination of the absorption coefficients of the primary and secondary radiations allows the following estimates to be made. (*a*) The lower limit of the average energy of the secondary radiation is about 30 million volts. (*b*) The average number of secondaries per primary is about 100 in iron and 230 in lead. (*c*) The energy of a primary cosmic ray, equal to the sum of the energies of its secondaries, is about 2×10^{10} volts.

PHOTOELECTRIC AND THERMIONIC EMISSION FROM COMPOSITE SURFACES.

BY

WAYNE B. NOTTINGHAM,*

Massachusetts Institute of Technology.

Classical methods when applied to photoelectric and thermionic emission from composite surfaces often lead to inconsistent results. A study of the thermionic emission, with a new thyratron circuit for heating tungsten and thoriated tungsten filaments, reveals that many points can be explained if we take into consideration the complex form of the potential barrier produced by an atom layer of electropositive metal when deposited on an " electronegative " base. From an experimental knowledge of the transmission coefficient of the barrier as a function of electron energy and the use of the Wentzel approximation for the transmission coefficient $D(v) = \exp - (4\pi/h \int_{x_1}^{x_2} (2mH)^{1/2} dx)$, it is possible to calculate the shape of the barrier which turns out to be practically parabolic and about 4.3×10^{-8} cm. in width one electron-volt below the top of the hill. Since the width and

* Abstract of paper published in the *Physical Review*, **41**, 793 (1932), and representing results of experiments performed as a fellow of the Bartol Research Foundation.

perhaps the height of the barrier seem to depend upon the temperature, it becomes clear that the Richardson-Dushman equation $I = AT^2 \exp(-b_0/T)$ is applicable only as an empirical representation of the data obtained with composite surfaces as emitters. This surface model explains very naturally the fact that the electrons emitted from a composite have an apparently Maxwellian distribution of velocities corresponding to a temperature fifty per cent. higher than that of the filament as reported by Koller and Rothe. It also gives a qualitative explanation of the observed dependence of the photoelectric long wave-length limit on the applied potential for thin films of sodium on nickel using very low fields.

PARTICLE IONIZATION FOR VELOCITIES APPROACHING THAT OF LIGHT.[1]

BY

W. F. G. SWANN and A. BRAMLEY.

The ionization produced by high speed β particles traversing an atmosphere of hydrogen has been calculated by Carlson and Oppenheimer [2] using Dirac's equation for the electron and by Williams,[3] by empirically improving Bethe's results for slow speed β particles,[4] to take account of the crowding up of the field of the β particle when its velocity becomes very close to that of light. These two methods, give results which are identical and predict that for high speed particles the ionization should increase indefinitely as the velocity of the β particle approaches the velocity of light. They neglect, however, considerations which, on the classical theory would be concerned with the radiation reaction on the electron ejected in the ionization. The effect of radiation on the classical theory has been considered by W. F. G. Swann [5] who has given reasons for supposing that, on that theory, ionization should cease at electron energies of the order 10^9 volts.

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[1] Abstract of a paper reported at the June, 1932, meeting of the American Physical Society at New Haven, Conn. (See *Phys. Rev.*, **41**, 393, 1932).

[2] *Phys. Rev.*, **38**, p. 1788, 1931.

[3] *Proc. Roy. Soc.*, **135**, p. 108, 1932.

[4] *Ann. der Phys.*, **5**, p. 325, 1930.

[5] *Phil. Mag.*, **47**, p. 308, 1924.

Following a method which is suggested by the results obtained by Williams we have taken the Schrödinger wave equation for the collision problem as formulated, e.g. in Bethe's paper, and instead of using for the mutual potential energy V an expression of the form $1/R$, we have replaced this term by a term which takes into account the crowding up of the lines of force, namely, $1/R(1 - \sin^2 \lambda)^{1/2}$. The introduction of a term of this form for V, leads to results which are in agreement with those of Williams. The integrations which are necessary before we can obtain a value for the ionization have not yet been carried out to completion but they indicate at the present time a result which should not differ appreciably from that of Williams. The use of Schrödinger's equation does not invalidate the results if we restrict our interest to the production of slow speed secondary electrons.

The effect of radiation reaction on the emitted electron in the classical problem for very high β particle energies suggests an analogous effect in wave mechanical theory, and suggests therefore the founding of a wave mechanical ψ equation upon a classical model which takes radiation and allied phenomena into account.

Classical electrodynamics gives, for small velocities, an equation of electronic motion of the forms:

$$\frac{e}{6\pi ac^2}\ddot{x} - \frac{e}{6\pi c^3}\dddot{x} + \cdots = E + \frac{[uH]}{c}$$

where a is the classical electrodynamic electronic radius; we can find a solution for $\ddot{x}$ of the form

$$\frac{e}{6\pi ac^2}\ddot{x} = E + \frac{[uH]}{c} - \left(\frac{a}{c}\right)\frac{dE}{dt} + \cdots,$$

which can be written in the form of the Hamiltonian equations with

$$H = \frac{m}{2}(\dot{q})^2 - \frac{2e}{c}\left\{1 - \frac{a}{c}\frac{d}{dt}\right\}\{\phi\dot{q}\},$$
$$+ e\left\{1 - \frac{a}{c}\frac{d}{dt}\right\}\{\phi\} + \cdots$$

where ϕ is the scalar potential and where the vector potential

U has been replaced by $\frac{v}{c}\phi$, with v the velocity of the high energy β particle.

For the problem of the collision of a high energy β particle with a hydrogen atom d/dt is replaced by $\partial/\partial t$ and this in turn by $-v\Delta$.

We have used this form of a Hamiltonian to calculate the ionization produced by high energy β particles. The introduction of the term in a/c causes the ionization to decrease practically to zero, when the speed of the β particles becomes of the order of 10^{10} to 10^{11} electron volts.

The form of Schrödinger's equation corresponding to this Hamiltonian resembles somewhat the second order equation which can be obtained from a consideration of the spin orbit interaction energy. The spin orbit interaction leads to an equation with a term $\frac{e}{2mc^2}(E \times \dot{q})S$ where S is the angular momentum of the electron spin. This term turns out to be negligible compared with the term $ae\left\{\frac{v}{c}\right\}\frac{\partial\phi}{\partial x}$, here introduced, partly because $\dot{q}/v$ is small and partly because

$$E = -\frac{1}{c}\partial U/\partial t - \frac{\partial\varphi}{\partial x} = -\left(1 - \frac{v^2}{c^2}\right)\partial\varphi/\partial x,$$

is small when v approaches c.

The question of whether or not the total ionization does decrease for very high energy β particles is not known at the present time; but an experimental decision of the matter presents a problem of profound interest in connection with possible ionization by cosmic rays considered as electrons of sufficiently high energy to reach the earth, at the equator in opposition to the earth's magnetic field.

THE FRANKLIN INSTITUTE.

STATED MONTHLY MEETING, OCTOBER 19, 1932.

The meeting was called to order at eight-fifteen p.m. by President Nathan Hayward.

The Secretary announced that one of the newspapers of the city had requested permission to take a straw ballot at the opening of the meeting.[1] This request having been granted, the first item of business was the taking of the ballot.

The Secretary announced that the last meeting of the Institute was the regular Medal Day meeting which was held in May and that the minutes of that meeting had been published in full in the JOURNAL of the Institute during the summer. He stated further that unless objection were offered, the minutes would be approved as printed. No objection was uttered and the minutes were declared approved.

The Secretary expressed the regret of the Board of Managers at the death of a considerable number of the members of the Institute during the summer months, and especially at the death of three very long time members, notably, Mr. Hugo Bilgram, Mr. Samuel T. Bodine and Professor Monroe B. Snyder. These gentlemen were among the members of longest standing in the Institute and were highly honored. Notices concerning these members will be published in the JOURNAL.

The Secretary then made a statement concerning the progress on the erection of the new building on the Parkway and expressed gratification at the great rapidity which had been displayed in recent weeks. He announced that the laying of the corner stone would be held in about a month and that it was now expected that the new institution would be open in about one year, and at the latest at the end of 1933.

There being no further business, the President presented as the speaker of the evening Dr. Thomas S. Johnson, Assistant Director of the Bartol Research Foundation of The Franklin Institute, who spoke delightfully on "Cosmic Radiations: Theory and Experimentation." Dr. Johnson's talk was accompanied by striking experimental demonstrations and was greatly enjoyed by the audience.

After some discussion the meeting adjourned at nine-thirty-seven p.m.

HOWARD MCCLENAHAN,
Secretary.

[1] To gather statistics regarding the coming presidential election.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, October 5, 1932.)

HALL OF THE COMMITTEE,
PHILADELPHIA, OCTOBER 5, 1932.

MR. EDWARD L. CLARK *in the Chair.*

The following reports were presented for first reading:

No. 2943: Work of Doctor Reginald A. Fessenden.
No. 2947: Non-Winding Clock.
No. 2955: Railway Car Cushion Underframe.
No. 2958: Planetarium.

The following Minute on the death of Mr. Hugo Bilgram was presented and adopted:

In the death of Hugo Bilgram at his home in Moylan-Rose Valley, on August 27, 1932, The Franklin Institute has lost an outstanding member, and the Committee on Science and the Arts an irreplaceable coworker.

Mr. Bilgram was born at Memmingen, Bavaria, January 13, 1847; was graduated from the Augsburg Maschinenbau Schule in 1865 where he studied Mechanical Engineering; came to America in 1869 and soon thereafter became an American citizen.

He became a member of The Franklin Institute September 20, 1872 and was elected a member of the Committee on Science and the Arts June 16, 1873. He served the Committee as Chairman during the year 1906 to 1907.

For more than fifty years Mr. Bilgram was the active head of the Bilgram Machine Works, during which time no product left his plant without having a high degree of accuracy.

In 1883 he invented and built the first Bevel Gear Generator—a device for which he received the award of the Elliott Cresson Medal in 1887. This invention established his reputation and the Bilgram gears are recognized as of the highest accuracy.

In 1929, those carrying on experiments for the production of sound moving pictures adopted the use of the Bilgram gear cutting machine which they found cut finer gears and increased the noiseless properties of them.

Mr. Bilgram had many hobbies—microscopy, botany, geology and finance. Nothing pleased this kindly, courteous octogenarian more than to sit at the head of a revolving table loaded with microscopes and explain the objects under super-observation.

He was the author of several books:

"Slide Valve Gears" 1878
"Involuntary Idleness" 1889
"Study of the Money Question" 1894
"Cause of Business Stagnation" 1905
"Cause of Business Depressions" 1914

The last book was in collaboration with Mr. Louis Edward Levy.

In one of his works he clearly pointed out the grave defects in our present system of finance and predicted a period of world-wide depression resulting therefrom, if not corrected.

He was an early member of the American Society of Mechanical Engineers, the Engineers' Club, Philadelphia Technischer Verein and American Academy of Political and Social Science.

Mr. Bilgram's membership in the Committee on Science and the Arts extended uninterruptedly for nearly sixty years which exceeds the next longest membership by ten years. During that time he seldom missed a meeting and his thorough knowledge and wide experience was of inestimable value to the work of the Committee.

The members of the Committee hereby express their high appreciation of their association with Mr. Bilgram in the Committee for many years and

Resolve, That the Committee on Science and the Arts hereby record its deep regret at the death of Mr. Hugo Bilgram and express its sympathy with his family in their loss.

And Further Resolve, That this report be spread upon the Minutes of the Committee on Science and the Arts and a copy sent to Mr. Bilgram's family.

GEO. A. HOADLEY,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, October 19, 1932.)

RESIDENT.

MR. FRANK P. BROWN, Plumber (Retired), Philadelphia, Pa.
MR. LEWIS G. SCHLEHNER, Building Superintendent, Elkins Park, Pa.

NON-RESIDENT MEMBERSHIP.

MR. GEORGE B. ALLEN, Chief Engineer, Dodge Brothers Corporation, Grosse Pointe Park, Mich.
REV. GEORGE F. STROHAVER, S. J., Department of Chemistry, Georgetown University, Washington, D. C.

CHANGES OF ADDRESS.

MR. CARL G. BARTH, 6484 Woodcrest Avenue, Philadelphia, Pa.
COLONEL EDWIN M. CHANCE, 1401 Arch Street, Philadelphia, Pa.
MR. WILLIAM CHANNING CUSHING, 5400 Greene Street, Philadelphia, Pa.
MR. FREDERIC A. DELANO, 1621 New Navy Building, 18th Street and Constitution Ave., Washington, D. C.
MR. E. A. FAIRMAN, Casella Co., Magallanes, Chile, South America.
MR. JOSEPH D. R. FREED, 35 Gateway Drive, Great Neck, L. I., New York.
MR. HARRY A. GOULD, 236 West Walnut Lane, Germantown, Philadelphia, Pa.
MR. NATHAN HAYWARD, JR., 85 Brattle Street, Cambridge, Mass.
MR. JOHN J. L. HOUSTON, 231 North 18th Street, Philadelphia, Pa.

MR. EARL L. KOCH, 4938 North Talman Avenue, Ravenswood Station, Chicago, Illinois.
DR. FRED W. KRANZ, 4215 Drury Lane, Fort Wayne, Indiana.
MR. HENRICK VON Z. LOSS, University Club, 1601 Locust Street, Philadelphia, Pa.
MR. OTTO T. MALLERY, 1427 Pine Street, Philadelphia, Pa.
MR. MATTHEW F. MAURY, University Club, 1601 Locust Street, Philadelphia, Pa.
MR. RICHARD L. MCCALL, Belgravia, 1811 Chestnut Street, Philadelphia, Pa.
MR. DANIEL E. MORAN, 370 Lexington Avenue, New York City, N. Y.
MR. A. SAUNDERS MORRIS, 114 St. Pauls Road, Ardmore, Pa.
DR. FREDERIC PALMER, JR., Haverford College, Haverford, Pa.
MR. F. N. PEASE, 1307 Third Avenue, Altoona, Pa.
MR. CHARLES PENROSE, c/o Day and Zimmermann, Inc., 620 Packard Building, Philadelphia, Pa.
DR. SAMUEL E. POND, Box 204, Woods Hole, Mass.
MR. ERNEST R. RECHEL, Grant Avenue and Tacony Street, Torresdale, Pa.
MR. ALEXANDER E. REOCH, c/o Radio Corporation of America, 570 Lexington Avenue, New York City, N. Y.
MR. JAMES S. ROGERS, 1414 Lincoln-Liberty Building, Philadelphia, Pa.
MR. JOHN M. RUSBY, 59 Booth Lane, Haverford, Pa.
DR. DAVID B. RUSHMORE, Room 1901, 14 Wall Street, New York City, N. Y.
MR. W. L. SAUNDERS, 2ND, Bryn Mawr, Pa.
MR. HORACE W. SELLERS, 1301 Stephen Girard Building, Philadelphia, Pa.
MR. JOHN STONE STONE, 1636 Torrence Street, San Diego, Calif.
MR. HARRY R. VAN DEVENTER, 45 East 51st Street, New York City, N. Y.
MR. WILLIAM R. WEBSTER, Hamilton Court, 39th and Chestnut Streets, Philadelphia, Pa.
MR. JOHN S. WILSON, c/o J. J. Bryan, Esq., 58 Simpson Avenue, Pitman, New Jersey.

NECROLOGY.

Mr. R. H. Ballard, Los Angeles, Calif.
Mr. W. L. Dempsey, St. Louis, Mo.
Mr. J. L. Ketterlinus, Philadelphia, Pa.
Dr. Joseph Leidy, II, Philadelphia, Pa.
Prof. M. B. Snyder, Philadelphia, Pa.

LIBRARY NOTES.

RECENT ADDITIONS.

BANNEITZ, F. Taschenbuch der drahtlosen Telegraphie und Telephonie. 1927.
BOLL, MARCEL. Exposé Électronique des Lois de l'Électricité. 1932.
BROGLIE, LOUIS DE. Théorie de la Quantification dans la Nouvelle Mécanique. 1932.
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CURTIS, HARRY A., Editor. Fixed Nitrogen. American Chemical Society Monograph Series No. 59. 1932.

Eastman Kodak Company. How to Make Good Pictures. A Book for the Amateur Photographer, Seventeenth edition, revised. No date.

NEEDHAM, DOROTHY MOYLE. The Biochemistry of Muscle. 1932.

REDMAYNE, SIR R. A. S. Modern Practice in Mining. Volume V. Colliery Machinery and Its Application. 1932.

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Royal Society of London. Index to the Proceedings 1905–1930, and to the Philosophical Transactions 1901–1930. 1932.

UNGERER, ALFRED. Les Horloges Astronomiques et Monumentales les Plus Remarquables de l'Antiquité jusqu'à nos Jours. 1931.

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BOOK REVIEWS.

EXPOSÉ ÉLECTRONIQUE DES LOIS DE L'ÉLECTRICITÉ. Courants continu et alternatifs. Électromagnetisme et inductions. Réseaux de distribution. Emission et reception radioelectriques. Par Marcel Boll, 72 pages, illustrations, 15 x 24 cms. paper. Paris, Hermann et Cie., 1932. Price 15 francs.

History, remarks M. Boll in his introduction, is a perpetual repetition. The hostility of electrical engineers (it might be better termed "caution") against corpuscular conceptions will without doubt be short-lived. But that period of transition from the customary fundamental conceptions in dealing with electrical phenomena into harmony with electronic theory may be unreasonably extended. His aim in presenting this condensed review of established theorems in electricity and magnetism in accordance with modern theories which are now definitely incorporated into physical science is to accelerate this change. To paraphrase a currently used expression, his object is to make electrical engineers "electronically-minded," and bring about the adoption of the more rational electronic conception as a basis of their formulas.

Employing those methods which have become familiar to physicists and engineers who are occupied with apparatus with which thermionic tubes are used, the author deduces the laws of electricity and magnetism, so bringing before the reader, in concise form a uniform treatment of the entire field of electric and magnetic phenomena. The work is a timely and suggestive contribution in the exposition of electric theory.

L. E. P.

L'EXISTENCE DU NEUTRON. LA PROJECTION DE NOYAUX ATOMIQUES, PAR UN RAYONNEMENT TRES PENETRANT. Par Irene Curie et F. Joliot, 22 pages, 15 x 24 cms., paper. Paris, Hermann et Cie., 1932.

Some two years ago Bothe and Becker showed that certain light elements emit a penetrating *gamma*-radiation when they are bombarded by *alpha*-particles. This radiation, the authors of this report regard as of nuclear origin because its penetrating power is far greater than that of the characteristic radiations of the atoms considered. In that investigation the authors discern a new method of study of the properties of the nucleus. They have accordingly repeated these experiments with view, on the one hand, of determining the penetrating power of rays excited in light nuclei and to endeavor to deduce the corresponding quantic energies, and, on the other hand, to determine whether the radiations of high quantum value which thus can be produced artificially are capable of producing new effects in their passage into the substance. These investigations and the significant conclusions to which they lead are therein reported in detail.

L. E. P.

LES PRINCIPES PHYSIQUES DE LA THÉORIE DES QUANTA, par W. Heisenberg, Professeur de Physique Théorique a l'Université de Leipzig. Traduit de l'Allemand par MM. B. Champion et E. Hochard. Agrégés Préparateurs à l'École Normale supérieure. Preface de M. Louis de Broglie. Prix Nobel. x–126 pages, 16 x 25 cms., paper. Paris, Gauthier-Villars et Cie., 1932. Price forty francs.

Analogies which have been satisfactory in clarifying the concepts of pre-atomic physics have not proved so readily applicable in the visualization of the mechanism and functioning of the composite dynamic atom upon which the modern theory of radiation phenomena is based. It is therefore not surprising that an explanation of atomic physical processes in simple language has not been forthcoming. In the present critical review of the fundamental principles of the quantum theory, the author has been at pains to use only elementary formulas and calculations in so far as that has been possible, more formal and amplified deductions being reserved to an appendix. Fortunately, he observes, mathematics is not subject to the limitations of language, and it has been possible to invent a mathematical scheme, the quantum theory, which seems entirely adequate for the treatment of atomic processes. For visualization, we must be content with the imperfect analogies of the wave-picture or the particle-picture, or a judicious combination of the two.

To Professor Heisenberg must be accorded the distinction of having been the first to succeed in defining the true physical significance of the new mechanics by compelling us to abandon some of the most fundamental ideas of classical physics. Further, his name is indelibly associated with the principle of uncertainty which now apparently is unassailable whether regarded as proof of a certain ideal and fundamental indetermination of natural microscopic phenomena, or as an indication of the limitation of our conceptions of waves and particles.

The work is already well-known to American readers, being the substance of a series of lectures which the author delivered at the University of Chicago in the spring of 1929, a translation of which into English was published the following

year. Readers who may be familiar with French and not German will doubtless find the French translation helpful in elucidating shades of meaning in the rendition of the original text into English.

L. E. P.

INTRODUCTION TO THEORETICAL SEISMOLOGY, by J. B. Macelwane, S. J. and F. W. Sohon, S. J. Part II, Seismometry, by F. W. Sohon, S. J., Director, Georgetown University Seismological Observatory. ix–149 pages, 15.5 x 23.5 cms. New York, John Wiley and Sons, Inc., 1932. Price $2.75.

The Society of Jesus has long deserved the gratitude of the scientific world for the splendid contribution that it is making in the study of earthquakes. The authors of this work are two of the leaders in this study. Father Macelwane is professor of geophysics at St. Louis University, and director of the Central Station of the Jesuit Seismological Association. Father Sohon, as director of the famous observatory at Georgetown Univeristy, is the successor to the late Rev. F. A. Tondorf, S. J., a pioneer seismologist and probably one of the best known members of his Society, through his frequent earthquake reports appearing in the daily press.

Though numbered as Part II, Father Sohon's share of the work, "Seismometry," is the first to appear. Part I, by Father Macelwane, deals with geodynamics, and is now in preparation. No other book in English covers the same ground, and in view of the importance of the subject, not alone for students of earthquakes, but also for those concerned with seismic methods of geophysical prospecting, and studies of vibrations, the one under review is doubly welcome.

In the preface the author states that he hopes "that the book will enable the observer to understand the principles that underlie his instrument, and that he may be enabled to test it, keep it in adjustment, understand its shortcomings and give an intelligent account of its behavior." With the exceptionally complete equipment of the Georgetown Observatory, he is in a particularly fortunate position to do this.

The ten chapters of the book bear the following headings: Oscillatory Motion, The Horizontal Seismograph, The Vertical Seismograph, The Recorder, Amplification, Actual Magnification, Friction, Galvanometric Registration, The Onset of a New Phase, and The Tapping Test. In an appendix he treats of the identification of phases, which contains some of the most serious pitfalls even for an experienced seismologist, Zeissig's Method for determining epicenters, solution of spherical triangles and the stereographic projection. Eight tables and an index complete the volume. It is well printed and bound, and the publishers are fully justified in their description of the work as "An adequate treatment of the mathematical theory of the seismograph."

JAMES STOKLEY.

A TEXTBOOK OF PRACTICAL ASTRONOMY, Primarily for Engineering Students, by Jason John Nassau, Professor of Astronomy, Case School of Applied Science. x–226 pages, 15 x 23.5 cms. New York and London, McGraw-Hill Book Co., Inc., 1932.

As a member of the faculty of a leading technical school, Dr. Nassau is well able to appreciate the needs of the engineering student for a knowledge of practical

astronomy, and he has here produced the book which will give him that knowledge. But, the subtitle notwithstanding, the book is one which should have a very great popularity among all who wish to learn, without too much complication, of the use of astronomical instruments, such as the sextant, the transit and the zenith telescope, of methods of finding time, determination of latitude and longitude and the corrections that must be made to observations. Though a knowledge of descriptive astronomy is obviously highly desirable for anyone wishing to undertake the study of practical astronomy, Dr. Nassau, in the first few chapters, gives enough of the essentials of astronomy to make the book a self-contained unit. Sample pages from the American Ephemeris are included throughout the book and the problems are so arranged that the data contained in these sample pages may be used for their solution. Complete notes and computations are a further aid to the student. Specific and practical instructions for the use of the various instruments are given, and these are supplemented by the numerous excellent photographs, showing the sextant, the transit, etc., in actual use. The book is well printed and bound, and has an adequate index, all these factors combining to make it the best available work of its kind.

JAMES STOKLEY.

CHEMICAL PATENTS INDEX, a comprehensive and detailed index of the subject matter of specification and claims of United States patents and patent reissues granted during the decennial period 1915–1924 inclusive, covering the entire field of chemical technology, by Edward Chauncey Worden, First, Ph.C., B.S., M.A., F.C.S., F.L.S., volume 2, Index of subjects C, D, and E, 1190 pages, 17 x 25 cms. New York, Chemical Catalog Company, Inc., 1932. Price $25.00.

This work must be seen to be appreciated. Eleven hundred and ninety pages (count 'em!) and includes only the letters C, D, and E. Three more volumes to come; apparently we have seen nothing as yet. Almost forgot to point out that only the U. S. Patents issued in the years 1915–1924 inclusive are being considered in this present undertaking.

The contents of this volume are enough to dismay or delight the chemical patent searcher depending upon the subject and the temperament of the incumbent. To illustrate: On page 1043 there is a subject heading: "Potassium methylate for the manufacture of dye"; and as references 324 patents are cited. Such imposing columns of figures may serve a worthy purpose in other respects. Persons in their right mind surely would hesitate to spend time discovering the 325th method for using C-H-three-O-K (potassium methylate) as a possible dye intermediate.

The author praises highly the work of the typographers and rightly so as a glance at pages 685–713 will show. In looking over these pages along with a casual turning of the myriad leaves, one cannot help marveling at the tremendous amount of detailed work represented therein.

So complete is the indexing that a searcher may find almost instantly a list of those patents covering the subject in question. And, better still, such a list will be subdivided according to the material's use and mode of application. It is interesting to see just how many uses can be found for any particular substance. The

number of things (10 pages) that can be done with castor oil is a revelation to the uninitiated.

To summarize: Chemical Patent Index is a comprehensive and detailed index of the subject matter of specification and claims of United States Patents and Patent Reissues granted during the decennial period 1915–1924 inclusive, covering the entire field of chemical technology. This comprises the ramifications of patented inorganic and organic chemical processes and products as applied to biology, microscopy, botany, mineralogy, pharmacy, medicine, photography and dyestuffs in both the warlike and peaceful arts.

T. K. CLEVELAND.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 429, The N. A. C. A. Apparatus for Studying the Formation and Combustion of Fuel Sprays, and the Results from Preliminary Tests, by A. M. Rothrock, 19 pages, illustrations, 23 × 29 cms., Washington, Superintendent of Documents, 1932. Price ten cents.

This report describes the apparatus as designed and constructed at the Langley Memorial Aeronautical Laboratory, for studying the formation and combustion of fuel sprays under conditions closely simulating those occurring in a high-speed compression-ignition engine. The apparatus consists of a single-cylinder modified test engine, a fuel-injection system so designed that a single charge of fuel can be injected into the combustion chamber of the engine, an electric driving motor, and a high-speed photographic apparatus. The cylinder head of the engine has a vertical-disk form of combustion chamber whose sides are glass windows. When the fuel is injected into the combustion chamber, motion pictures at the rate of 2,000 per second are taken of the spray formation by means of spark discharges. When combustion takes place the light of the combustion is recorded on the same photographic film as the spray photographs.

The report includes the results of some tests to determine the effect of air temperature, air flow, and nozzle design on the spray formation. The results show that the compression temperature has little effect on the penetration of the fuel spray but does affect the dispersion, that air velocities of about 300 feet per second are necessary to destroy the core of the spray, and that the effect of air flow on the spray is controlled to a certain extent by the design of the injection nozzle. The results on the combustion of the spray show that when ignition does not take place until after spray cut-off the ignition may start almost simultaneously throughout the combustion chamber or at different points throughout the chamber. When ignition takes place before spray cut-off the combustion starts around the edge of the spray and then spreads throughout the chamber.

Report No. 430, Measurements of Flow in the Boundary Layer of a 1/40-Scale Model of the U. S. Airship "Akron," by Hugh B. Freeman. 15 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1932. Price five cents.

This report presents the results of measurements of flow in the boundary layer of a 1/40-scale model of the U. S. airship "Akron" ("ZRS-4") made with the object of determining the boundary-layer thickness, the point of transition

from laminar to turbulent flow, and the velocity distribution in the boundary layer.

The boundary-layer thickness was found to vary along the 19.62-foot hull from 0.08 inch at the most forward station, about 15 inches from the nose, to approximately 10 inches at the tail. A marked increase in the rate of thickening of the boundary layer was found at the transition from laminar to turbulent flow which occurred at a Reynolds Number $\left(\frac{Va}{\nu}\right)$ of about 814,000, where (a) is the axial distance from the nose. The velocity distribution over the greater part of the turbulent portion of the boundary layer was found to be fairly well approximated by the seventh-power law. The frictional drag, computed from the loss of momentum in the boundary layer and also from Clark Millikan's equations was in good agreement with the measured drag.

Report No. 431, Characteristics of Clark Y Airfoils of Small Aspect Ratios, by C. H. Zimmerman, 12 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1932. Price five cents.

This report presents the results of a series of wind-tunnel tests showing the force, moment, and autorotational characteristics of Clark Y airfoils having aspect ratios varying from 0.5 to 3.

An airfoil of rectangular plan form was tested with rectangular tips, faired tips, and semicircular tips. Tests were also made on one airfoil of circular plan form and two airfoils of elliptical plan form.

The tests revealed a marked delay of the stall and a decided increase in values of maximum lift coefficient and maximum resultant force coefficient for aspect ratios of the order of 1 as compared with the values for aspect ratios of 2 and 3. The largest value of $C_{R\,\max}$ was 2.17 with a wing of circular plan form and an aspect ratio of 1.27. The same wing gave a $C_{L\,\max}$ of 1.85 and an L/D ratio of 1.63 at 45° angle of attack.

Wings having aspect ratios of about 1 were found to have moment characteristics more favorable to stability than those having larger aspect ratios. Decreasing the aspect ratio greatly reduced ranges and rates of autorotation based on a given span and air speed. Results, when reduced to infinite aspect ratio by conventional formulas, indicate that such formulas are not applicable for aspect ratios less than 1.5. It is apparent that the plan form and tip shape of the wing are of major importance among the factors affecting airfoil characteristics at aspect ratios of 1.5 and smaller.

Report No. 432, Force Measurements on a 1/40-Scale Model of the U. S. Airship "Akron," by Hugh B. Freeman. 18 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1932. Price five cents.

This report describes a series of tests made on a 1/40-scale model of the U. S. airship "Akron" ("ZRS-4") for the purpose of determining the drag, lift, and pitching moments of the bare hull and of the hull equipped with two different sets of fins. Measurements were also made of the elevator forces and hinge moments.

The results of the drag measurements are in fair agreement with those of previous tests on smaller models of the "Akron" conducted in the variable-density tunnel of this laboratory. The type of tail surface designated Mark-II, a short wide surface, was found to have more favorable control characteristics than the long narrow type, Mark-I. The results of the measurements of the elevator hinge moments showed that the elevators for both types of fins were overbalanced for a large range of elevator angles, indicating that the area of the balancing vanes, for the Mark-II elevators at least, was excessive.

Report No. 433. Rates of Fuel Discharge as Affected by the Design of Fuel-Injection Systems for Internal-Combustion Engines, by A. G. Gelalles and E. T. Marsh. 15 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1932. Price five cents.

Using the method of weighing fuel collected in a receiver during a definite interval of the injection period, rates of discharge were determined, and the effects noted, when various changes were made in a fuel-injection system. The injection system consisted primarily of a by-pass controlled fuel pump and an automatic injection valve. The variables of the system studied were the pump speed, pump-throttle setting, discharge-orifice diameter, injection-valve opening and closing pressures, and injection-tube length and diameter.

The results show that, for the same orifice diameter, the rate of discharge increased with the pump speed and injection-valve opening and closing pressures. For the same pump speed, the throttle setting had little effect upon the rate of discharge up to the point of cut-off. The rates of discharge conformed approximately to the contour of the cam only with the larger size orifices; with the smaller orifices, because of the excess energy supplied by the pump over that utilized for discharge, the higher intensity reflections and reënforcements altered the discharge to a different conformation. The tube length was found to have little effect on either the rate of discharge, injection period, or injection lag. The data show that the pressure before the injection valve is affected substantially if injection-tube diameters are used that are below the critical diameter.

Report No. 434. Lift and Drag Characteristics and Gliding Performance of an Autogiro as Determined in Flight, by John B. Wheatley. 10 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1932. Price five cents.

The results of flight tests made by the National Advisory Committee for Aeronautics on a Pitcairn "PCA-2" autogiro are presented in this report. Lift and drag coefficients with the propeller stopped have been determined over approximately a 90° range of angles of attack. Based on the sum of fixed-wing and swept-disk areas, the maximum lift coefficient is 0.895, the minimum drag coefficient with propeller stopped is 0.015, and the maximum L/D with propeller stopped is 4.8. Lift coefficients were found also with the propeller delivering positive thrust and did not differ consistently from those found with propeller stopped. Curves of gliding performance included in this report show a minimum vertical velocity of 15 feet per second at an air speed of 36 miles per hour and a flight-path angle of $-17°$. In vertical descent the vertical velocity is 35 feet per second.

Report No. 435. Fuel Vaporization and its Effect on Combustion in a High-Speed Compression-Ignition Engine, by A. M. Rothrock and C. D. Waldron. 25 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1932. Price ten cents.

The tests discussed in this report were conducted to determine whether or not there is appreciable vaporization of the fuel injected into a high-speed compression-ignition engine during the time available for injection and combustion. The effects of injection advance angle, fuel boiling temperatures, fuel quantity, engine speed, and engine temperature were investigated. The results show that an appreciable amount of the fuel is vaporized during injection even though the temperature and pressure conditions in the engine are not sufficient to cause ignition either during or after injection, and that when the conditions are such as to cause ignition the vaporization process affects the combustion. The results are compared with those of several other investigators in the same field. The tests were conducted with the N. A. C. A. combustion apparatus.

Report No. 440. The Mechanism of Atomization Accompanying Solid Injection, by R. A. Castleman, Jr., 12 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1932. Price five cents.

A brief historical and descriptive account of solid injection is followed by a detailed review of the available theoretical and experimental data that seem to throw light on the mechanism of this form of atomization. It is concluded that this evidence indicates that (1) the atomization accompanying solid injection occurs at the surface of the liquid after it issues as a solid stream from the orifice; and (2) that such atomization has a mechanism physically identical with the atomization which takes place in an air stream, both being due merely to the formation, at the gas-liquid interface, of fine ligaments under the influence of the relative motion of gas and liquid, and to their collapse, under the influence of surface tension, to form the drops in the spray. This simple theory, previously proposed by the author, is the most satisfactory and fits the observations the best of any yet advanced. It is recommended that use of term "atomization" be restricted to a certain definite range, in which its use is sound, etymologically and physically.

FARADAY AND HIS METALLURGICAL RESEARCHES WITH SPECIAL REFERENCE TO THEIR BEARING ON THE DEVELOPMENT OF ALLOY STEELS, by Sir Robert A. Hadfield, Bt. xix–329 pages, illustrations, plates, portraits 16 × 25 cms. Cleveland, Ohio, The Penton Publishing Company, 1932.

Chromium steel, nickel steel, copper steel, silver steel, platinum steel, rhodium steel and gold steel, all these Faraday made. How do we know? Covered with the dust of more than a century, a box, 9 × 5½ × 5¼ inches, made of deal and containing seventy-nine specimens of steel and alloys was discovered tucked away in an obscure corner or nook of the Royal Institution. A label on this box read: "Faraday"—"Steel and Alloys." The seventy-nine pieces of metal had a total weight of only 7 lb. 14 oz.

Sir Robert A. Hadfield is a deserving recipient of our sincerest thanks. The mere writing of this book was an undertaking of noble proportion but even it takes

on the aspects of a sinecure when compared to the exacting task of examining over four-score specimens of Faraday's handiwork by the most improved methods of modern metallography. Such examination involved determinations of chemical constitution, polishing and photomicrographing the crystal structure, making spectroscopic, hardness, electrical and magnetic tests. This examination was even extended to the point of making miniature knives and a razor from certain of the alloys. In all, 434 chemical analyses were made requiring 6½ ozs. of drillings, each analysis using about fifteen thousandths of an ounce. Each specimen was photomicrographed and a considerable number of these prints add to the book's attractiveness. The author has seen fit to subject a few of the specimens to heat treatments thereby throwing further light upon the type of processing they had undergone in the hands of Faraday. Heating and cooling curves were made upon seven specimens; specific magnetism measurements upon twenty-two and the electrical resistance determined for three of the alloys. Faraday was indeed fortunate in being able to secure appreciable quantities of platinum, palladium and rhodium to alloy with his steel. There are in existence today specimens containing 48.6 per cent. platinum, 22.7 per cent. palladium, and 48.8 per cent. rhodium respectively. Only the rhodium alloy successfully resists the action of boiling sulfuric acid. None of the three could withstand hot hydrochloric acid and only the rhodium steel resisted nitric acid.

This book contains 329 pages and prospective readers may wonder just what all was used to fill up these 10,000 square inches of space. Suppose we turn quickly through the pages and get some idea of the subject matter. Chapter I: "Faraday, a Great Experimental Philosopher." The pioneer of research on special steels, publisher of 162 papers 6 of which dealt with metallurgy; excellent photographs of Faraday's deal box and the 79 steel specimens contained therein. Chapter II: "Faraday's Rise to Fame." Humble origin and ancestry, education as a chemist, connections with the Royal Institution, Royal Society, Faraday—the man, his influence on scientific advance, eulogies and medals. Chapter III: "The Stage and the Damatis Personae." The Royal Institution and biographical sketches of twenty Faraday contemporaries; excellent portraits embellish this chapter. Chapter IV: "Early Workers in Metallurgy." Chronological order of various discoveries, comparison of annual tonnages; what Sir Humphrey Davy knew about iron; India steel and Wootz metal, the Delhi Iron Pillar. Chapter V: "Sequence of Events." Factors inducing Faraday to undertake the production of alloys. Chapter VI: "The Birth of Alloy Steels." The elemental facilities available at that time, pyrometers, the blast furnace, crucibles and refractories; how Faraday prepared his alloys, his own account, his specific gravity determinations, heat treatments, corrosion tests and practical application of the alloys in the contempory arts. Chapter VII: "Modern Investigation of Faraday's Steel and Alloys." See second paragraph of this review. Chapter VIII: "Appreciation of Faraday's Work." Chapter IX: "Later Developments of Alloy Steels." History of alloy steel development, manganese steel, silicon steel, importance of steel alloys, annual output of iron, steel and alloy steels, economies from using alloy steels; the stories on: corrosion-resisting steels, high chromium-nickel steel, steam turbine blades, heat-resisting steels, high-speed tool steels, armament steel, special structural and high-tenacity steels, special magnetic alloys and importance

of heat treatment; what of the future? (The author's specialty is alloy steels and he is the inventor of a series of manganese steels.)

A short Chapter X—"Conclusion," completes the summary. The book is thoughtfully provided with an index. The fifty-eight plates represent a very choice collection of photographs and have added much to the attractiveness of the volume.

T. K. CLEVELAND

PUBLICATIONS RECEIVED.

Chemical Engineering Catalog, 1932 (Seventeenth Annual) Edition. Collected, condensed and standardized catalog data of equipment, machinery, laboratory supplies, . . . with classified indexes, . . . and a technical and scientific books section, . . . New York, The Chemical Catalog Company, Inc. 847 pages, illustrations, 21.5 × 28.5 cms.

Chemical Patents Index, a comprehensive and detailed index of the subject matter of specifications and claims of United States Patents, by Edward Chauncey Worden, volume two, Index of subjects, C, D and E, 1190 pages. 17 × 25 cms. New York, The Chemical Catalog Company, Inc., 1932. Price $25.00.

Vibration Prevention in Engineering, by Arthur L. Kimball, 145 pages, 15.5 × 23.5 cms. New York, John Wiley & Sons, Inc., 1932. Price $2.50.

Electric and Magnetic Fields, by Stephen S. Attwood, 314 pages, illustrations, 15.5 × 23.5 cms. New York, John Wiley & Sons, Inc., 1932. Price $3.50.

Elementary Qualitative Analysis for College Students, by J. H. Reedy, 2d edition, 163 pages, tables, illustrations, 14 × 21 cms. New York and London, McGraw-Hill Book Company, Inc., 1932. Price $1.50.

The Free Energies of Some Organic Compounds, by George Sutton Parks, and Hugh Martin Huffman, American Chemical Society Monograph Series, 251 pages, tables, illustrations, 15.5 × 23.5 cms. New York, The Chemical Catalog Company, Inc., 1932. Price $4.50.

Laboratory Physics, by Dayton Clarence Miller, 438 pages, tables, illustrations, 15 × 21 cms. Boston, Ginn & Company, Price $3.00.

International Handbook of the By-Product Coke Industry, by Prof. Dr. W. Gluud, American edition, based on revised German edition, by D. L. Jacobson, 879 pages, illustrations, tables, plates, 16 × 24 cms. New York, The Chemical Catalog Company, Inc., 1932. Price $15.00.

The Principles of Optics, by Arthur C. Hardy, and Fred H. Perrin, 632 pages, illustrations, tables, 15.5 × 24 cms. New York, McGraw-Hill Book Co., Inc., 1932. Price $6.00.

L'Azeotropisme la Tension de Vapeur des Melanges de Liquides, Bibliographie, par Maurice Lecat, 128 pages, 16 × 25 cms. Bruxelles, Maurice Lamertin, 1932.

Acoustics and Architecture, by Paul E. Sabine, 327 pages, illustrations, 15 × 23.5 cms. New York, McGraw-Hill Book Company, Inc., 1932. Price $3.50.

La Propagation des Ondes Electromagnetiques, Expose des Connaissances Acquises Syntheses des Idees et des Theories, par Paul Labat, 445 pages, illustrations, 16.5 × 25 cms. Paris, Gauthier-Villars et Cie, 1932. Price 80 francs.

Experimental Chemistry for Colleges, by J. Allen Harris, and William Ure, 191 pages, illustrations, 20.5 × 26.5 cms. New York, McGraw-Hill Book Company, Inc., 1932. Price $1.25.

United States Coast and Geodetic Survey, Results of Observations made at the United States Coast and Geodetic Survey Magnetic Observatory at Sitka, Alaska in 1925 and 1926, by Daniel L. Hazard, 100 pages, tables, maps, 19 × 27.3 cms. Washington, Government Printing Office, 1932.

National Advisory Committee for Aeronautics, Technical Notes, No. 431, Tests on Thrust Augmentors for Jet Propulsion, by Eastman N. Jacobs and James M. Shoemaker, Langley Memorial Aeronautical Laboratory, 4 pages, illustrations, 20 × 26 cms. Washington, Committee, 1932. No. 432, Drag Tests of 4/9-Scale Model Engine Nacelles with Various Cowlings, by Ray Windler, Langley Memorial Aeronautical Laboratory, 11 pages, tables, illustrations, 20 × 26 cms. Washington, Committee, 1932.

CURRENT TOPICS.

Dangerous Depilatory.—(U. S. Department of Agriculture Clip Sheet No. 739.) Not so long ago the newspapers announced that a concern which manufactured a well-known depilatory (hair remover) had filed a plea of bankruptcy. And, considering the nature of the chemical used in this preparation, it is small wonder the company ended thus. The depilatory contained an extremely injurious chemical, thallium acetate, which is a virulent poison. The preparation, to be rubbed upon parts of the body, had caused severe illness in a number of cases.

It is unfortunate the Federal Food and Drug Administration has no control over a preparation of this sort which falls into the category of cosmetics and is neither a food nor a drug. Cosmetics are subject to the law only if they are labeled for the cure, mitigation, or prevention of disease.

C.

MK (Magnet) Steel.—In the July 1932 issue of Ohm, a Japanese magazine devoted to electrical engineering, announcement is made of the perfection of a new series of magnet steels by Dr. T. Mishima, an Assistant Professor at the Tokyo Imperial University of Tokyo, Japan. These new magnet steels are characterized by a very high order of permanence. The coercive force is claimed to be about nine times that of the usual tungsten magnet steels and two and one-half times that of the best cobalt magnet steels.

The MK steels consist mainly of iron, nickel and aluminum. A typical composition is 25 per cent. nickel, 10 per cent. aluminum and the balance iron. Alloys, such as these are not readily forged and must be cast into the desired form. However, their desirable magnetic properties are developed by simple annealing and they are free from the difficulties of quenching which is required with the tungsten steels. The magnetic properties do not change appreciably with increases in temperature of even several hundred degrees Centigrade. They are also said to be magnetically stable when subjected to mechanical vibration or shocks.

C.

Sweet Laxative.—Most persons who have attained their majority can recall way back when the taking of a laxative was a " man's

job" and a parent's ingenuity was taxed to the limit before the offspring could be coaxed to add another one of "Life's Darkest Moments" to the juvenile calendar. Now, through the efforts of several manufacturers the taking of such correctives has been rendered quite pleasurable at least to the inherently sweet-toothed child. Too much so it might seem. The U. S. Department of Agriculture Clip Sheet No. 741 tells of a healthy 10-year-old boy who recently ate the contents of a box of a well-known laxative tablet, mistaking them for candy. The boy's temperature rose rapidly, he became delirious, and died nine days later.

Dr. F. J. Cullen of the Federal Food and Drug Administration refers to this unfortunate happening in pointing out the necessity for the user of a drug to read carefully the label. Manufacturers generally are labeling laxatives and cathartics in full compliance with the law. However, one should not relax in the matter of keeping such attractively prepared drugs out of the reach of children too young to realize their full significance.

C.

Some Are Stains.—(U. S. Department of Agriculture Clip Sheet No. 741.) The Bureau of Home Economics publishes some timely advice on how to remove summer stains. Peach stains contain tannin and are best removed by first soaking the spot in warm glycerin. If the fabric is white cotton or linen, follow with oxalic acid solution, rinse, and neutralize with ammonia. Warm glycerin can be used equally well on colored fabrics but should be followed with denatured alcohol, not oxalic acid. Many fruit and berry stains on white cotton and linen can be taken out easily by stretching the fabric over a large bowl, and pouring boiling water on the spot from a teakettle held high above it.

Oxalic acid will sometimes take out mildew stains that resist soap and water. Mildewed cotton shower curtains may be bleached by soaking in Javelle water. (Never use Javelle water on silk, wool or colored goods.)

C.

The Briny Deep.—Since depressions have been receiving more than their usual share of attention these last few years, it might not be inappropriate to mention a few that may well boast an eonic immunity from the handiwork of man. *Science News Service* informs us the Hydrographic Office has published officially a summary of the deepest "deeps" in each ocean.

The greatest known ocean depth is in the Pacific: the Mindanao Deep, 35,400 feet, near the Philippine Islands. The pressure at this

depth would be over 7½ tons per square inch. This great deep was discovered in 1929 by the new German Cruiser "Emden." In the South Pacific the greatest depth is the Aldrich Deep, north of New Zealand, 30,930 feet. The deepest sounding known in the North Atlantic is Nares Deep, approximately 27,972 feet, in West Indian Waters. The deepest spot in the South Atlantic is a sounding of 26,575 feet made in 1926 by the German survey ship "Meteor." This is far out at sea, the nearest land being the forsaken island of South Georgia, east of the southern tip of South America.

The other oceans show lesser depths than this. The Indian Ocean has the Wharton Deep, about 22,968 feet, south of Java and east of Cocos Island. A sounding of 17,850 feet was made in the Arctic Ocean by Sir Hubert Wilkins in 1927, and a depth of 14,274 in the Antarctic is shown by a British Admiralty chart. It is interesting to learn the ocean is not so deep at the poles, but if the earth's rotation is considered, such relative shallowness in the vicinity of the polar axes seems logical.

C.

Temperature's Nadir.—*Science News Service* reports that scientific workers, with the consumption of much time and labor, have approached one-tenth degree nearer the point of absolute temperature. Prof. W. H. Keesom of Leiden University has succeeded in producing a temperature of minus 272.3 degrees Centigrade which is within seven or eight-tenths of zero temperature absolute depending upon whether such a point is accepted as corresponding to 273 or 273.1 degrees Centigrade below the freezing point of water (0° C.).

It seems very improbable that absolute zero shall ever be attained. The secret of such low temperatures lies in removing heat from the system at a faster rate than it can be absorbed from its surroundings. The rate of heat removal depends upon the velocity of the molecules of the substance being cooled and since this velocity decreases with the temperature, theoretically at least, the molecules should be motionless at absolute zero. If such be true the rate of attainment of this ultimate cold point should finally become infinitely small corresponding to the infinitely slow rate of molecular movement.—Prof. Keesom obtained his low temperature by keeping a small quantity of liquid helium constantly stirred while he produced a high vacuum over it by means of a pair of powerful mercury pumps.

Effect of Acids Upon Paper.—The U. S. Dept. of Agriculture has found that acids, even in minute quantities, cause papers to

"age" and deteriorate so that they crack when folded. To libraries and to governmental and business offices which must preserve written and printed records for long periods, this aging of papers has been a problem of importance never satisfactorily solved.

The general method of sizing paper is to mix thoroughly into the pulp a preparation of emulsified rosin and possibly starch, clay and other finely divided fillers. When the cellulose pulp has absorbed the rosin and other materials alum is added to react with the rosin and precipitate it solidly upon the fiber. Alum is acid by nature and unless the water in which the pulp is suspended contains approximately 0.25×10^{-3} per cent. of sulfuric acid a complete precipitation of the sizing material will not be attained. As will be seen, this small amount is not apt to damage the paper appreciably.

However, should the addition of alum not be carefully controlled, too great a concentration of acid may occur and the life of the paper cut short. Thus, tests made on a strong, unsized, all-rag bond paper showed no decrease in strength after being artificially aged by heat for 336 hours at 100° C. On the other hand, sulfuric acid present in as small quantities as 0.033 per cent. caused about 19 per cent. loss in strength as measured by folding endurance, while 0.074 per cent. decreased the strength about 99 per cent. Alum (aluminum sulfate) had practically the same effect as sulfuric acid compared on a basis of equivalent acidity. The coating of paper helps to offset liability of damage by acid since most coatings are slightly alkaline by nature and a consequent neutralization of the acid results.

C.

Krypton.—The chemical aloofness of krypton apparently has been overcome. *Science Service* reports that three physicists of the Chemical Institute at Bonn have forced this recalcitrant member of the rare gases into its first known chemical union. These Bonn experimenters seem to have produced a compound of krypton and chlorine. The former gas was circulated by means of a pump at a pressure of one to five per cent. of atmospheric and kept at the temperature of liquid air. As the gas was circulated through a glass tube it was subjected to an electric discharge and at the same time chlorine gas was introduced. Coincident with a fall in pressure, a dark-red substance appeared and is believed to be a krypton chloride compound. Argon, another rare gas, failed to respond to similar treatment.

C.

An Electrical Conductor of Sodium.—The members of the American Electrochemical Society meeting at Cleveland, O., were told about a conductor of metallic sodium, four inches in diameter, that is being used to carry as much as 4,000 amperes of electric current. Readers acquainted with the properties of sodium will realize there is something wrong with this picture.—It should have been added that the sodium was enclosed in an iron pipe. Sodium, left in contact with the atmosphere, widely combines with oxygen, moisture and carbon dioxide to give caustic soda and sodium carbonate. Placed in water, this active element rapidly generates hydrogen and sufficient heat to combine the latter with oxygen with explosive force.

Although the resistance of sodium is three times that of copper, it weighs only one-ninth as much. To carry the same amount of current, a sodium conductor must have almost three times the cross-sectional area as one of copper.

C.

Pine or Hickory for Fuel? (U. S. D. A. Clip Sheet No. 744).—Pound for pound, pine wood gives off more heat than hickory. But, since wood is purchased by the cord (volume), rather than by weight, a cord of hickory probably will furnish the more heat. And so we are right back where we started.

C.

Dust Explosions.—It would seem that under suitable conditions explosions may be produced by the dust of any combustible substance. This was emphasized in an impressive manner by the U. S. Dept. of Agriculture before members of the National Safety Council Congress. Grain elevator dust, soap powder, starch dust, milk powder, sugar dust, wood charcoal dust, wood dust and cork dust, all were exploded in a miniature factory. These tests demonstrated methods of protecting manufacturing plants against structural damage by releasing dust explosion pressures through adequate vents.

The safety codes for dust explosion prevention in grain handling and manufacturing as developed by the Dept. of Agriculture have decreased the average loss for each such explosion from approximately $520,000 in 1921 to about $28,000 in 1931.

The Soybean (U. S. D. A. Clip Sheet No. 745).—The soybean promises to become America's most versatile crop—highly valuable both industrially and agriculturally. The U. S. Dept. of Agricul-

ture has recently completed a collection of nearly 400 soybean products from the Orient as well as America.

The collection of products is divided into the four groups according to whether their origin lies in the flour, bean, meal or the oil. In the flour group are bread, cakes, macaroni, vermicelli, noodles, spaghetti, infant foods, diabetic foods, and beverages such as malted milks. From the bean proper are soy sauce, sprouts, bean milk in fresh, powdered, and canned forms, bean cheese, flour, soybean butter, and meat substitutes. The meal provides animal food such as poultry, hog, cattle and dog feed, glue, fertilizers, and flour. The oil has proved a fertile field for development and from it are made soaps, ink oils, salad oil, shortening, core oil used in foundries, rubber substitutes, disinfectants, paint, varnish, chocolate candy, and lecithin, a phosphatic tonic compound. Besides the oil uses adopted in America, the Orientals use it to make candles and waterproof goods. Another significant product is a fuel oil made from soybean oil by the Japanese. This is not commercially profitable now but indicates a possible future development.

C.

Cause of Mottled Enamel.—MARGARET CAMMACK SMITH, EDITH M. LANTZ, AND H. V. SMITH (University of Arizona, College of Agriculture, Agricultural Experiment Station Tech. Bull. No. 32, 253–282, 1931; *Jour. Dental Research*, 1932, xii, 149–159) attribute the occurrence of mottled enamel, an endemic disease of the teeth, to the presence of an abnormally high concentration of fluorides in the drinking water. In Arizona, these lesions do not occur in communities whose water supply contains 0.3 milligram or less of fluoride anion per liter, and are endemic in localities whose water supply contains between 3.8 and 7.15 milligrams of fluoride anion per liter. The lesions are produced experimentally in rats by (1) use of natural drinking water rich in fluorides, or (2) incorporation of the total solids of such water in the ration, or (3) addition of sodium fluoride to the ration.

J. S. H.

New Hormone.—N. B. LAUGHTON AND A. BRUCE MACALLUM (*Proc. Royal Soc.*, B, 1932, cxi, 37–46) have discovered, in the mucous membrane of the intestine, a hormone which exerts a specific stimulating action on the secretion of insulin by the islets of Langerhans in the pancreas. Its action, however, is limited to animals with a normal pancreas, for it has no influence on the concentration of sugar in the blood in animals from which the pancreas has been removed.

J. S. H.

Classification of Hemicelluloses.—L. F. HAWLEY AND A. GEOFFREY NORMAN (*Ind. and Eng. Chem.*, 1932, xxiv, 1190–1194) divide the hemicelluloses into the polyuronides and the cellulosans. The polyuronides are incrusting substances not closely associated with the cellulose and practically always contain a uronic acid, such as blucuronic acid and galacturonic acid. The cellulosans are very intimately associated with the cellulose, never contain a uronic acid, and are represented by such compounds as xylan and mannan.

J. S. H.

Atomic Weight of Silicon.—PHILIP F. WEATHERILL AND PERRY S. BRUNDAGE (*Jour. Am. Chem. Soc.*, 1932, liv, 3933–3938) have redetermined the atomic weight of silicon by hydrolysis of silicon tetrachloride in an aqueous solution of hydrochloric acid, and measurement of the ratio silicon dioxide: silicon tetrachloride. The atomic weight of silicon was then calculated from this ratio, and was found to be 28.103 ± 0.0027.

J. S. H.

Bittersweet Seed.—CHARLES BARKENBUS AND CHARLES F. KREWSON (*Jour. Am. Chem. Soc.*, 1932, liv, 3993–3997) have made a chemical study of the seed of the bittersweet, *Celastrus scandens*, whose fruit is widely used as a decoration. The yield of lipins varied with the solvent, being 36.06 per cent. with petroleum ether of boiling point 50° to 60° C., 46.72 per cent. with ether, and 53.22 per cent. with ethyl alcohol (95 per cent.). Among the constituents present in the seed meal after extraction of the lipins with absolute ether were:—Moisture 3.05 per cent., ash 2.88 per cent., crude protein 18.94 per cent., crude fiber 9.14 per cent., preformed invert sugar 0.49 per cent., invertible sugar 1.60 per cent., pentosans 5.87 per cent., starch 0.68 per cent. The extracted lipins formed a medium yellow clear oil with a bland taste and a slight agreeable odor; among its constants were:—Specific gravity at 20° C. 0.9772, index of refraction at 20° C. 1.4815, iodine number (Hanns) 121.5, thiocyanogen iodine number 69.96, safonification number 297.07, Reichert-Meissl number 70.86, acid value 3.98, acetyl value 147.5, unsaponifiable matter (per cent.) 2.96, soluble acids (calculated as per cent. butyric acid) 18.98, Hehner number 70.94, hexabromide number of the insoluble acids 17.66, unsaturated acids (corrected per cent.) 57.13, insoluble saturated acids (corrected per cent.) 9.83. The oil contained glycerides derived from organic acids as follows:—Linolic acid 38.46 per cent., linolenic acid 21.03 per cent., oleic acid 0.25 per cent., palmitic acid 8.42 per cent., stearic acid 1.88 per cent., formic, acetic and caproic acids 15.67 per cent.; it is

uncertain that the last three acids actually are present as glycerides. The presence of these acids (formic, acetic, and caproic) gives rise to the extremely high Reichert-Meissl number, as well as the unusual values of several other constants.

J. S. H.

Micro Determination of Nitrogen.—L. N. LAPIN AND W. E. KILL (*Zeit. klin. Medizin*, 1931, xcviii, 278–285) convert the nitrogenous compounds (for instance, those present in a protein-free blood filtrate) into ammonium sulphate by a modified Kjeldahl digestion. The resulting mass is dissolved in 20 cc. of distilled water, and mixed with 10 cc. of a modified Nessler solution and 2 cc. of Fehling solution. The resulting green solution is transferred to a porcelain dish. In a similar dish, a blank is prepared, containing the same volumes of Kjeldahl digestion reagent, and Nessler and Fehling solutions, and having the same total volume as the determination proper. A solution of ammonium chloride, containing 0.1 milligram of ammoniacal nitrogen per cc., is added to the blank from a micro burette until the blue color changes to the same shade of green as occurs in the determination proper. The blank then contains the same mass of nitrogen as is present in the sample used in the determination proper.

J. S. H.

Chlorocruorin.—This pigment, which is red in concentrated solution and green in dilute solution, occurs dissolved in the blood plasma of certain polychaete worms, and resembles hemoglobin in properties and in chemical composition. H. MUNRO FOX (*Proc. Royal Soc.*, B, 1932, cxi, 356–363) has studied chlorocruorin, obtained from the worm *Spirographis spallanzanii*, by means of a spectrophotometer. He concludes that, at the temperature at which this worm lives, the chlorocruorin has an affinity for oxygen of the same order of magnitude as the affinity of hemoglobin for oxygen in the human body.

J. S. H.

Volatility of Tincture of Iodine.—Tincture of iodine may lose volatile constituents as a result of loosening of the stopper. This may be brought about by storage in a warm place and the resulting increase in pressure exerted by the contents of the bottle upon the stopper, or by prolonged action of the iodine upon the cork stopper and the resulting contraction of the cork. J. G. ROBERTS (*Am. Jour. Phar.*, 1932, civ, 635–636) exposed samples of the tincture, measuring 50 cc. and contained in wide mouth flasks, to the action

of the atmosphere for periods as great as 7 days. At the end of that time, the volume had decreased to 29 cc., and 46.27 per cent. of the alcohol and 6.6 per cent. of the iodine initially present had been lost. The iodine concentration in the residual liquid was considerably greater than the iodine concentration in the original tincture.

J. S. H.

Wax-like Coating of the Apple.—K. S. MARKLEY, STERLING B. HENDRICKS, AND CHARLES E. SANDO (*Jour. Biol. Chem.*, 1932, xcviii, 103–107) have examined the petroleum ether extract of the wax-like coating of the apple. The bulk of the extract was normal nonacosane ($C_{29}H_{60}$); a secondary alcohol, 10-nonacosanol, was also present. Ketones were not present in isolable quantities.

J. S. H.

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